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Diversity-Oriented Synthesis of Enantiomerically Pure Steroidal Tetracycles Employing Stille/Diels–Alder Reaction Sequences

Hans Wolf Sünnemann,[a] Martin G. Banwell,[b] and Armin de Meijere*[a]

Abstract: Various steroid analogues were synthesized by Stille coupling of bicyclo[4.3.0]nonenylstannanes *cis*-/*trans*-**8** and **14** with cyclohexenol triflates **17** and **18** and subsequent Diels–Alder reactions of the resulting dienes. The enantiomerically pure bicyclo[4.3.0]nonenylstannanes *cis*- and *trans*-**8** were prepared in good yields via the enol triflates *cis*- and *trans*-**7**, obtained from the bicyclo[4.3.0]non-2-en-3-one **5**. The alkenylstannane **14** was obtained from the [2+2] cycloadduct **10a** produced from addition of dichloroketene to the enantiomerically pure and protected bishydroxycyclohexadiene **9a** (65%). Treatment of **10a** with diazomethane, reduction of the dichloromethylene group, and trapping with tributyltin chloride after lithium-for-bromine exchange, yielded the bicyclo[4.3.0]nonenylstannane **14** (23% over four steps). Stille couplings provided the tricyclic dienes *cis*-/*trans*-**19** in good yields (73–77%), whereas the tricyclic diene **20** was obtained in only 34% yield at best. Diels–Alder reactions of *trans*-**19** with various reactive dienophiles yielded the novel steroidal compounds *trans*-**21** to *trans*-**26** with complete diastereoselectivity. Heating the dienes *cis*-**19** or **20** with maleic acid derivatives provided the corresponding tetracycles *cis*-**23**α,β and **27**α,β with a *cis*-C,D ring junction, each as mixtures of two diastereomers. Less reactive dienophiles required higher temperatures to promote the relevant cycloaddition with *trans*-**19** to furnish several stereoisomeric forms of *trans*-**28** and *trans*-**29** in significantly lower yields (31–45%). The selected steroid analogues *trans*-**22** and *trans*-**23** were deprotected in two steps by using acid catalysis to provide *trans*-**31** and *trans*-**33** (91 and 80% over two steps). Cyclopropanation of *trans*-**30** yielded the cyclopropasteroid analogue **34** (74%), treatment of which with trifluoroacetic acid furnished the cyclopropasteroid **35** and the 2-methyl-substituted steroid analogue **36** in 40 and 12% yield, respectively. Aromatic B-ring steroids **38** (69%) and **39** (5%) were accessed by dehydrogenation of *trans*-**24** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Keywords: catalysis · cross-coupling · Diels–Alder reaction · palladium · steroids

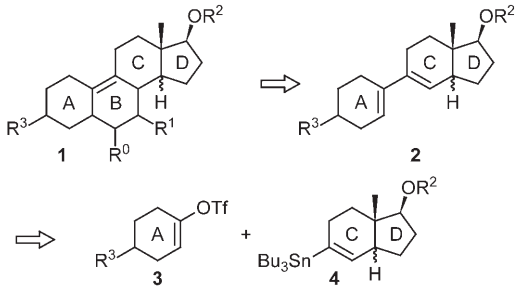
Introduction

Natural steroids and many of their analogues are important substances with a wide spectrum of biological activities including pharmacologically relevant ones.[1] Exploiting both natural and novel synthetic steroids for use as potential pharmaceuticals is, therefore, a highly promising research area in medicinal chemistry.[2,3] However, the therapeutic application of steroidal compounds is sometimes accompanied by undesired physiological side effects.[4]

Appropriate structural modifications to steroids can lead to improved therapeutic indices and, therefore, fewer or less intense physiological side effects.[5] To develop a deeper understanding of the structure–activity relationships within the class, a larger number of structurally diverse steroids would have to be investigated. These can be best obtained by total synthesis. Interestingly, many classical steroid syntheses are highly target-oriented and often only lead to single compounds.[5] In view of the demands of pharmaceutical research, an efficient, diversity-oriented steroid synthesis would be of considerable interest. Therefore, a new approach to the tetracyclic steroidal framework following a convergent A+CD→ACD→ABCD synthetic strategy was designed (Scheme 1). The retrosynthetic concept for this is based on three building blocks for the A-, C,D-, and B-rings which, by permutation, allows for a high degree of diversity.

[a] Dr. H. W. Sünnemann, Prof. Dr. A. de Meijere
Institut für Organische und Biomolekulare Chemie der
Georg-August-Universität Göttingen, Tammannstrasse 2
37077 Göttingen (Germany)
Fax: (+49) 551-399475
E-mail: Armin.deMeijere@chemie.uni-goettingen.de

[b] Prof. Dr. M. G. Banwell
Research School of Chemistry, Institute of Advanced Studies
The Australian National University
Canberra ACT 0200 (Australia)



Scheme 1. Retrosynthetic depiction of a new approach to the steroid skeleton.

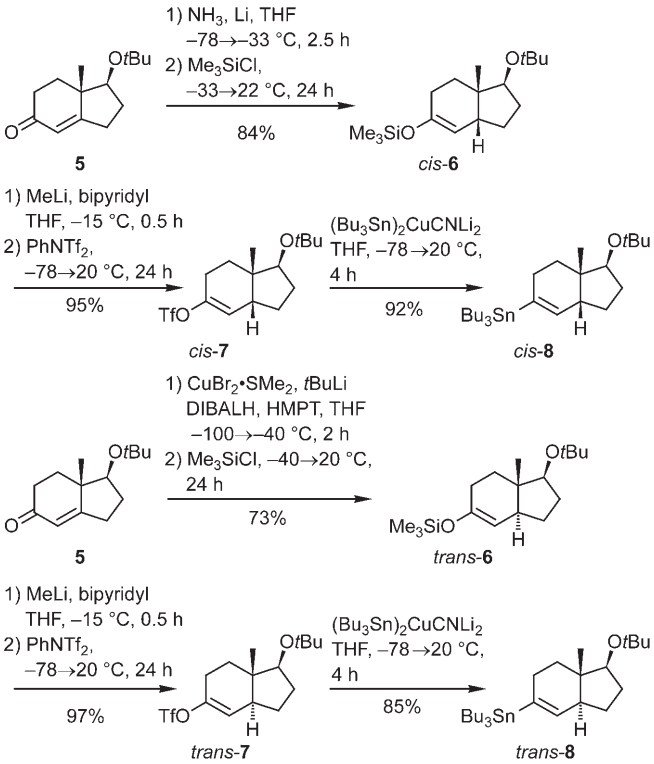
The C,D-rings would be linked to the A-ring by a Stille cross-coupling reaction, and the B-ring finally completed by using a Diels–Alder reaction. This approach would lead to steroidal compounds with substituents at C-6 and C-7, a substitution type that has rarely been achieved,[6] but nevertheless appears to be a particularly interesting one.[7]

Results and Discussion

The necessary building blocks resembling the C,D-ring system of the final steroid are bicyclo[4.3.0]non-2-enylstannanes of type *cis*-**8** and *trans*-**8**. The syntheses of these start from the readily available and enantiomerically pure Hajos–Parrish–Wichert–Sauer ketone **5** (Scheme 2).[8] Reduction with lithium in liquid ammonia and THF as a cosolvent, followed by trapping of the so-formed lithium enolate with chlorotrimethylsilane provided the enol silyl ether *cis*-**6** with a *cis*-ring junction in 84% yield.[9]

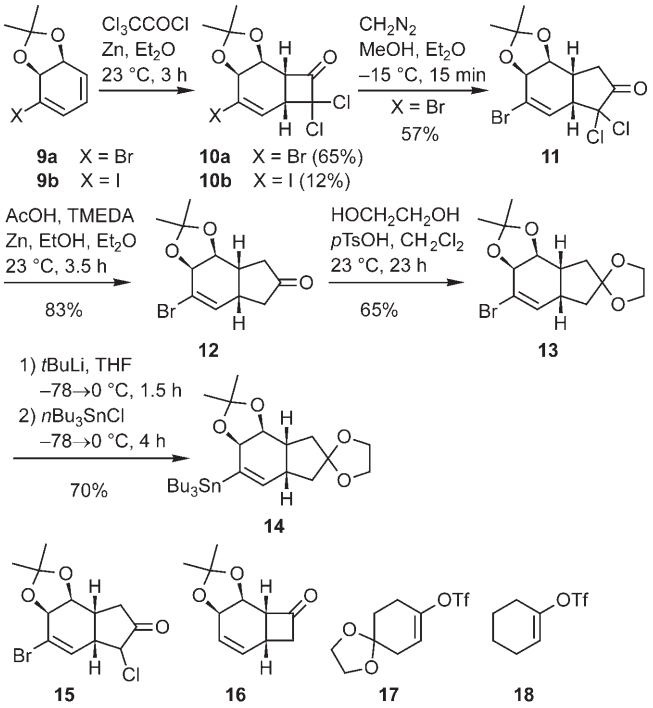
The corresponding *trans*-isomer (*trans*-**6**) was obtained by reduction of compound **5** with a copper hydride complex generated in situ from cuprous bromide–dimethyl sulfide complex, diisobutylaluminum hydride, and *tert*-butyllithium. Trapping of the resulting enolate with chlorotrimethylsilane then gave *trans*-**6**.[10] For optimal diastereoselectivity, the hexahydroindenone **5** had to be added very slowly. After cleavage of the enol silyl ethers *cis*-**6** and *trans*-**6** with methyllithium in the presence of 4,4′-bipyridyl and trapping of the resulting enolates with *N*,*N*-bis(trifluoromethanesulfonyl)aniline,[11] the bicyclo[4.3.0]nonenol triflates *cis*-**7** and *trans*-**7**, respectively, were obtained in excellent yields of 95 and 97%, respectively.[9] The enol triflates *cis*-**7** and *trans*-**7** reacted smoothly with dilithium bis(tri-*n*-butylstannyl)cyanocuprate[12] to yield the tri-*n*-butylbicyclo-[4.3.0]nonenylstannanes *cis*-**8** and *trans*-**8** in 92 and 85% yield, respectively (Scheme 2).

To extend this methodology so as to be able to access corticosteroid analogues, the enantiomerically pure bicyclo-[4.3.0]nonenylstannane **14** was synthesized from the protected 1-halo-5,6-dihydroxycyclohexa-1,3-dienes **9a**,**b**, which are readily accessible by microbial oxidation[13] of the corresponding halobenzene and subsequent protection of the resulting diol (Scheme 3).[14] [2+2]-Cycloaddition of in situ



Scheme 2. Bicyclo[4.3.0]nonenylstannanes *cis*-/*trans*-**8** as basic building blocks for the new steroid synthesis. DIBALH = diisobutylaluminum hydride; HMPT = hexamethylphosphoric triamide.

generated dichloroketene[15] to **9a**,**b** led to the oligofunctionalized bicycles **10a**,**b**. The iodocyclohexadiene **9b** partially decomposed under the reaction conditions, which resulted in compound **10b** being obtained in only 12% yield. However, under optimized conditions, the bromodiene **9a** furnished the desired bicycle **10a** in 65% yield along with the product of a [4+2] cycloaddition (Scheme 3). At temperatures below 0°C, the [2+2] cycloaddition did not take place at an observable rate. Reductive removal of only one of the chlorine substituents from **10a** under established conditions (Zn–Cu, MeOH, NH_4Cl, RT)[16] could not be achieved, instead some of the fully dehalogenated bicycle **16** was obtained among several other unidentified products. However, ring-enlargement of the dichlorocyclobutanone moiety within **10a** with diazomethane in the presence of methanol proceeded smoothly to provide the tetrahydroindanone derivative **11** in 57% yield.[17] The two chlorine atoms were then cleanly removed with zinc and acetic acid in the presence of tetramethylethylenediamine to provide the tetrahydroindanone **12** (83%).[18] Interestingly, treatment of **11** with zinc and ammonium chloride selectively furnished the monochlorotetrahydroindanone **15** as a single diastereomer of undetermined configuration at the chlorinated carbon center. The carbonyl group within **12** was protected as the corresponding 1,3-dioxolane **13**, which was obtained by treatment of **12** with ethylene glycol under *p*-toluenesulfonic acid catalysis. To achieve acceptable yields (65%), the reaction had to be performed by using low concentrations of **12**,



Scheme 3. A novel protected 4,5-dihydroxy-8-oxobicyclo[4.3.0]non-2-en-3-ylstannane **14** as a building block for corticosteroid analogues. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; *p*Ts = *p*-toluenesulfonyl.

otherwise a significant fraction underwent cleavage of the acetonide moiety. The lithium-for-bromine exchange on **13** with *tert*-butyllithium was relatively slow, and for this to go to completion, the reaction mixture had to be warmed to −20 °C and eventually to 0 °C to destroy excess *tert*-butyllithium. The alkenyllithium species was trapped with tri-*n*-butyltin chloride to yield the bicyclo[4.3.0]nonenylstannane **14** (70 %) (Scheme 3).

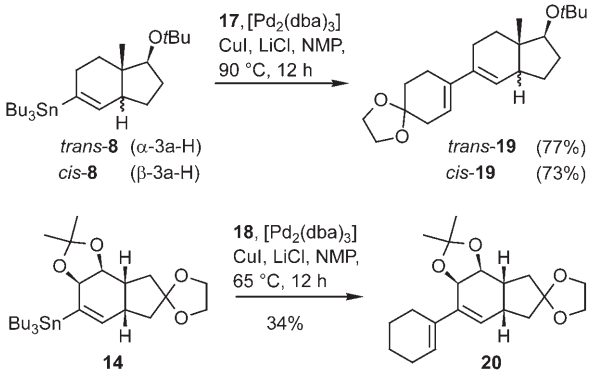
The necessary Stille-coupling substrates representing the A-rings in the targeted steroidal skeletons, specifically the enol triflates **17** and **18**,[19] were prepared from cyclohexane-1,4-dione monoethylene acetal and cyclohexanone, respectively, according to a modified protocol employing sodium bis(trimethylsilyl)amide (prepared from inexpensive sodium hydride[20] and bis(trimethylsilyl)amine) to generate the respective enolate, and trifluoromethanesulfonic acid (triflic) anhydride in diethyl ether to trap the enolate. Unlike THF, diethyl ether turned out to be stable towards the triflic anhydride at −20 °C. Thus, the enol triflate **17** was obtained in 96 % yield.

Stille couplings[21] of the enol triflates **17** and **18** with the bicyclo[4.3.0]nonenylstannanes *cis*-**8**, *trans*-**8**, and **14** yielded the tricyclic 1,3-dienes *cis*-**19**, *trans*-**19**, and **20**. Tetrakis-(triphenylphosphine)palladium proved to be inefficient as a catalyst for the Stille coupling of **17** with *trans*-**8**. The supposedly more-reactive catalyst based on dipalladiumtris(dibenzylideneacetone)·chloroform decomposed prematurely. However, with added cuprous iodide and lithium chloride, the tricyclic diene *trans*-**19** could be obtained in 57 % yield (Table 1, entry 2). To achieve such yields, the solvent *N*-methylpyrrolidone had to be completely anhydrous. The yields, based on the starting enol triflate **17** (Scheme 4),

Table 1. Stille couplings of cyclohexenol triflates **17** and **18** with bicyclo-[4.3.0]nonenylstannanes.

Entry	Vinyl-stannane	Enol t	riflate	Catalyst [mol %][a]	*T* [°C]/*t* [h]	Product	Yield [%][b]
1	*trans*-**8**	**17**	C (5)	65/12	*trans*-**19**	–[c]	
2	*trans*-**8**	**17**	A (5)	90/12	*trans*-**19**	57	
3	*trans*-**8**	**17**	A (5)	90/12	*trans*-**19**	77[d]	
4	*cis*-**8**	**17**	A (5)	90/12	*cis*-**19**	73[d]	
5	**14**	**18**	A (5)	65/12	**20**	–[c]	
6	**14**	**18**	B (5)	65/12	**20**	34	

[a] A: $[Pd_2dba_3]$·$CHCl_3$, CuI, LiCl, NMP; B: as in A, plus 1.00 equiv CuI; C: as in A, plus $AsPh_3$. [b] Isolated yields. [c] Complete decomposition of the starting material. [d] The vinylstannane was used in 20 % excess.



Scheme 4. Stille coupling reactions leading to tricyclic dienes *cis*-**19** and *trans*-**19** as well as **20**. dba = dibenzylideneacteone; NMP = *N*-methylpyrrolidone.

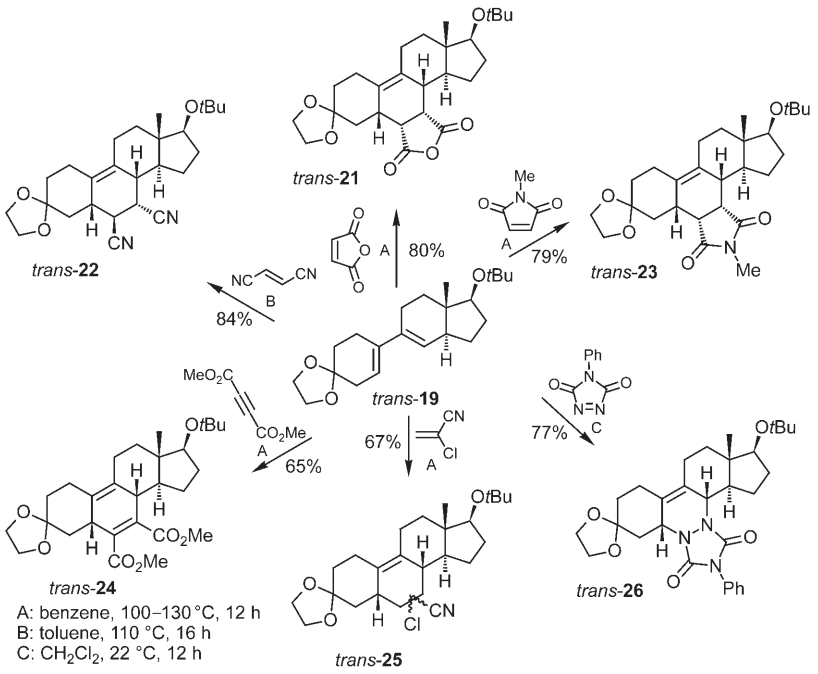
could be further improved to 77 and 73 % for *trans*-**19** and *cis*-**19**, respectively, by employing the bicyclo-[4.3.0]nonenylstannes *cis*-**8** and *trans*-**8** in 20 % excess (entries 3,4). It is noteworthy that the addition of triphenylarsine, which is known to enhance the transmetallation rate in Stille couplings,[22] led, in the case of *trans*-**8** and **17**, to a rapid decomposition of the starting material and/or the product (entry 1).

This optimized catalyst system was not able to bring about the coupling of cyclohexenyl triflate **18** with the novel bicyclo[4.3.0]nonenylstannane **14**. This outcome can be explained by the presence of the sterically demanding acetonide unit adjacent to the reacting alkenyltin moiety. Apparently, there is no rate acceleration induced by coordination effects of the neighboring oxygen atom towards the metals involved, namely palladium and copper. However, after the addition of one equivalent of CuI, the reactants could not be detected anymore and the tricyclic diene **20** was isolated in 34 % yield, which proved to be sufficient for testing **20** in Diels–Alder reactions. As for the coupling of the alkenylstannane *trans*-**8**, after addition of $AsPh_3$ to the reaction

mixture, significant decomposition of the starting material was observed.

The abovementioned and previously unreported tricyclic dienes **19** and **20** are reasonably well set up for subsequent Diels–Alder reactions to furnish compounds embodying the steroid framework.

Upon treatment with maleic anhydride in benzene at 100 °C, *trans*-**19** cleanly furnished the steroid analogue *trans*-**21** in 80 % yield, and with *N*-methylmaleimide at 100 °C the cycloadduct *trans*-**23** was obtained in 79 % yield. Both cycloadditions followed the *endo* rule of Alder and gave single diastereomers. The absolute configuration of *trans*-**21** was established by an X-ray crystal structure analysis[19] (see Figure 1), and the same was done for the single diastereomer *trans*-**22** that was formed in 84 % yield upon cycloaddition of fumaronitrile onto *trans*-**19** which occurred in toluene at 110 °C (Scheme 5).[23]



Scheme 5. Diels–Alder reactions yielding novel enantiomerically pure steroidal compounds.

4-Phenyl-1,2,4-triazoline-3,5-dione, which is well known for its high dienophilicity, reacted with *trans*-**19** in methylene chloride at ambient temperature to yield *trans*-**26** (77 %), also as a single diastereomer. The less reactive dimethyl acetylenedicarboxylate (DMAD), like the other dienophiles employed, required heating in benzene and gave *trans*-**24** (65 % yield), a steroidal compound with a 1,4-diene moiety in the B-ring. It is noteworthy that the yield of *trans*-**24** was only 23 % when toluene was used as solvent. On the other hand, heating of *trans*-**19** with DMAD in chlorobenzene as an electron-deficient aromatic solvent did not furnish *trans*-**24** in better yield.[24] The unsymmetrically substituted dienophile 2-chloroacrylonitrile gave a mixture of two regioisomeric cycloadducts of *trans*-**25** in a yield of 67 %.

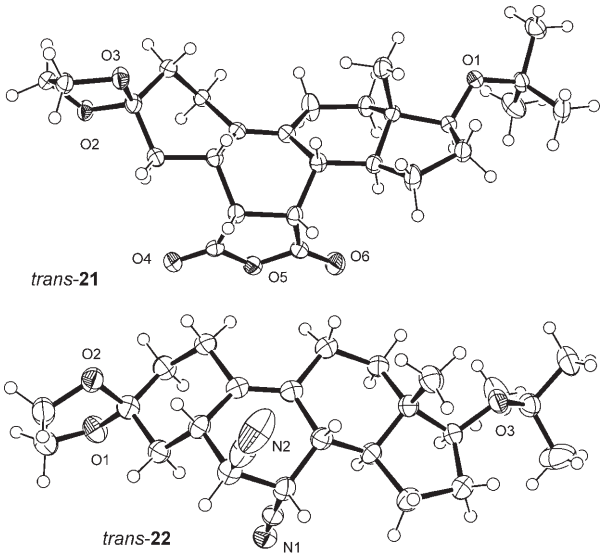


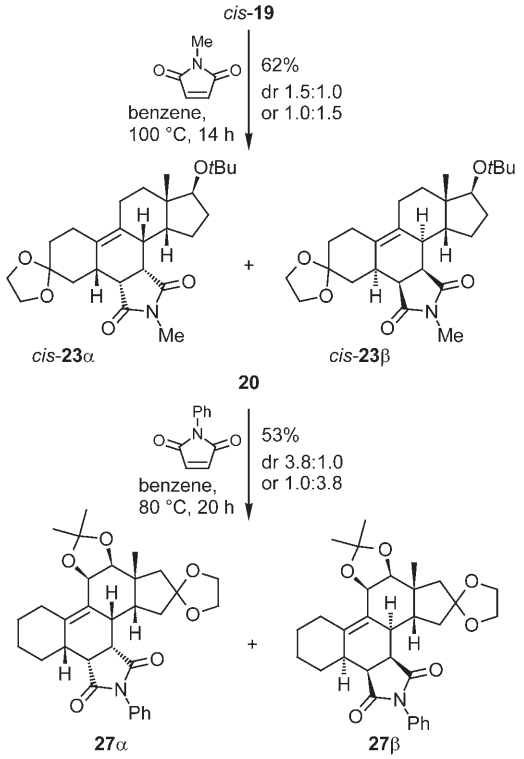
Figure 1. X-ray crystal structure analyses of the steroid analogues *trans*-**21** and *trans*-**22**.[24]

Unlike *trans*-**19**, the diene *cis*-**19** did not react diastereoselectively with *N*-methylmaleimide. Due to the bent molecular shape, the directing effects of the methyl group at C-13 and the *tert*-butoxy substituent at C-17 apparently are not as dominant so that both diastereomers *cis*-**23**α and *cis*-**23**β can be formed by approach of the dienophile to either face of the molecule with comparable ease (1:1.5). Nevertheless, both diastereomers (62 %) are again *endo*-Diels–Alder adducts (Scheme 6).

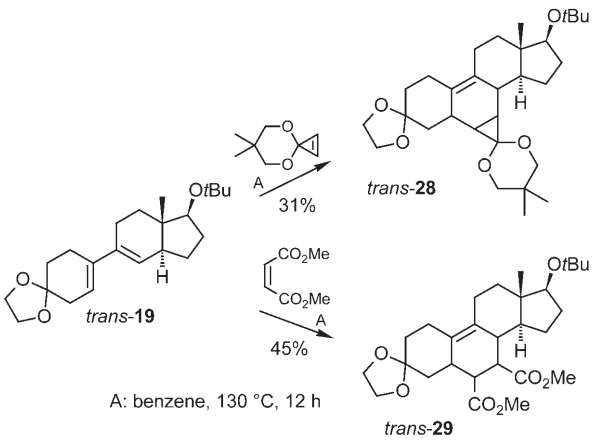
The diastereoselectivity was slightly more pronounced (3.8:1) in the cycloaddition of *N*-phenylmaleimide onto the more highly functionalized diene **20**, which also has a *cis*-junction at its bicyclo[4.3.0]nonene core. The two diastereomeric adducts **27**α and **27**β were isolated in a combined yield of 53 %.

The less-reactive dienophiles dimethyl maleate and 6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-ene required heating at 130 °C for their cycloadditions onto *trans*-**19** to occur at reasonable rates and the products *trans*-**28** and *trans*-**29**, (31 and 45 % yields, respectively) were each mixtures of several diastereomers (Scheme 7).[25]

Attempts to accelerate the Diels–Alder reaction of methyl acrylate with *trans*-**19** by adding ethylaluminum dichloride were not successful, as no reaction occurred at low



Scheme 6. Diels–Alder reactions of the tricyclic dienes *cis*-**19** and **20** with *N*-methyl- and *N*-phenylmaleimide, respectively.

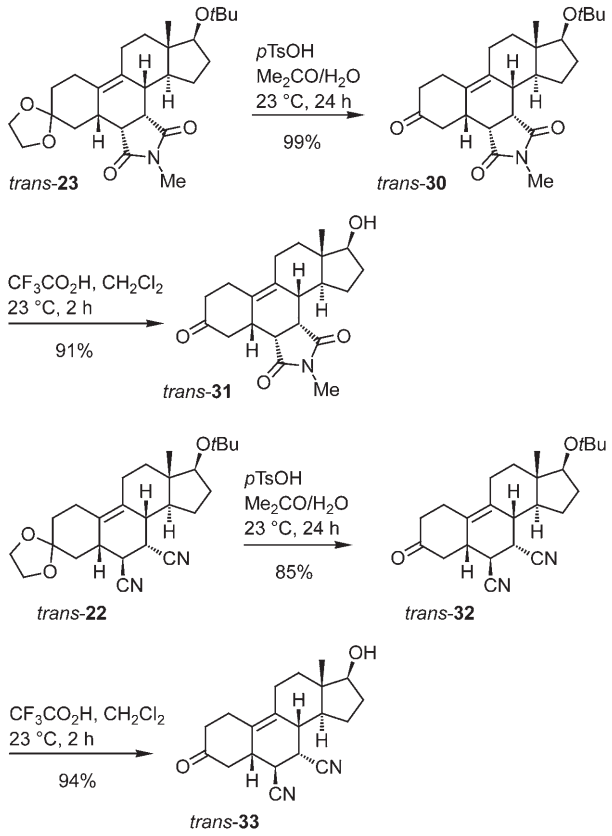


Scheme 7. Diels–Alder reactions of the tricyclic diene *trans*-**19** with a cyclopropane acetal and dimethyl maleate.

temperatures (−78 °C), while decomposition of the substrates was observed at ambient temperature.

Due to the stereoselectivity of the Diels–Alder reaction, the resulting steroidal frameworks do not have a naturally occurring configuration. Instead, one carbon atom or another always has the inverted configuration. Therefore, the novel approach described here provides access to different epimers of the natural steroid skeleton. As such, they should be interesting subjects for biological investigations (Schemes 5–7).

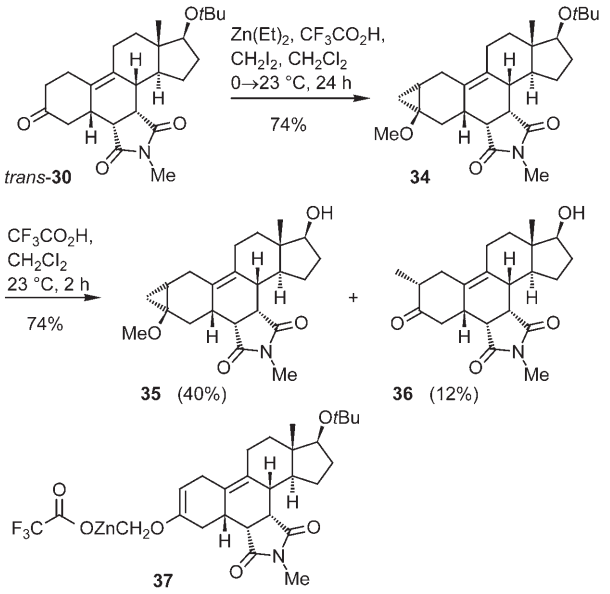
To demonstrate the capability of the new steroid synthesis to provide samples for biological testing, the protecting groups within compounds *trans*-**22** and *trans*-**23** were removed in two steps. The 1,3-dioxolane moieties were cleanly cleaved with *p*-toluenesulfonic acid in aqueous acetone to furnish the oxosteroids *trans*-**30** (99 %) and *trans*-**32** (85 %). On the other hand, the *tert*-butyl ether moieties were best cleaved with trifluoroacetic acid in methylene chloride. Thus, the steroid analogues *trans*-**31** and *trans*-**33** were obtained, with conservation of the original configuration, in 91 and 94 % yield, respectively (Scheme 8).[26]



Scheme 8. Deprotection of selected steroid analogues.

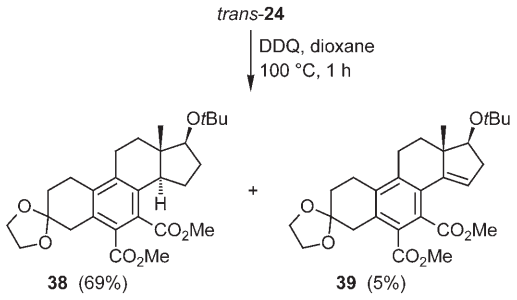
Attempts were made to cyclopropanate the tetrasubstituted double bond in *trans*-**30** with the trifluoroacetoxy-activated zinc carbenoid generated from diiodomethane and diethylzinc according to Shi et al.[27] However, the central double bond remained untouched and, instead, the methoxycyclopropane-annelated derivative *trans*-**34** was obtained in 74 % yield. Apparently, the initially formed iodomethylzinc trifluoroacetate reacted with the enol of *trans*-**30** to form the zinc-substituted enol methyl ether *trans*-**37**, and this was subsequently cyclopropanated by an excess of the zinc carbenoid to furnish, after hydrolysis, the diastereomerically pure steroidal hexacycle *trans*-**34**. Attempts to cleave the *tert*-butyl ether within *trans*-**34** provided the cyclopropasteroid *trans*-**35**[28] as the major product (40 %), but this was accompanied by *trans*-**36**, the α-methyl derivative of *trans*-**30**

resulting from cyclopropane ring opening,[29] as a single diastereomer in 12% yield. 2,3-Cyclopropane-annelated steroid analogues of type *trans*-**35** have been found to act as irreversible inhibitors of cholesterol oxidase,[30] and the minor product *trans*-**36** is structurally similar to anabolic-androgenic steroids (Scheme 9).[31]



Scheme 9. Attempted cyclopropanation of the tetrasubstituted double bond within *trans*-**30**.

Dehydrogenation of the steroidal diene *trans*-**24** with DDQ,[32] afforded a mixture of the B-ring aromatic tetracycle *trans*-**38** (69% yield) as the major product[33] and *trans*-**39** with an additional double bond in the D-ring as the minor product (5%; Scheme 10).[34]



Scheme 10. New steroid analogues with an aromatic B-ring obtained by dehydrogenation of the steroidal diene *trans*-**24** with DDQ. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

All of the new steroidal products described herein ought to be enantiomerically pure because the bicyclo[4.3.0]nonenylstannane building blocks *trans*-**8** and *cis*-**8** were enantiomerically pure starting materials; almost all the transformations occurred with complete diastereoselectivity and without any possible racemization of the preset stereogenic centers.

Conclusion

A sequence of Stille cross-coupling reactions of cyclohexenol triflates with enantiomerically pure bicyclo[4.3.0]nonenylstannanes and subsequent Diels–Alder reactions of the resulting tricyclic 1,3-dienes leads efficiently to novel steroid analogues with interesting functionalities for further elaboration. The thus obtained steroidal tetracycles with a *trans*-C,D-ring junction were single diastereomers, whereas the analogues with a *cis*-C,D-ring junction were mixtures of two diastereomers each. With less-reactive dienophiles, the steroid analogues so-formed were mixtures of several diastereomers. Overall, a spectrum of new steroid analogues, which includes examples with an aromatic B-ring and with a cyclopropane-annelated A-ring, are accessible in good yields. Removal of protecting groups could be readily achieved and provided sufficiently large samples for biological testing. As this new access to the steroid skeleton is based on three variable building blocks, the diversity of obtainable steroidal compounds is of particular interest.

Experimental Section

General remarks: ^{1}H NMR: Bruker AM 250 (250 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to chloroform ($\delta = 7.26$ ppm) or benzene ($\delta = 7.20$ ppm) as internal reference. ^{13}C NMR: Bruker AW 250 (62.9 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to chloroform ($\delta = 77.0$ ppm) or benzene ($\delta = 128$ ppm); the multiplicities of the signals were determined by the DEPT (62.9 MHz) technique and are quoted as (+) for CH_3 and CH groups, (−) for CH_2 groups and (C_{quat}) for quaternary carbon atoms. IR spectra: Bruker IFS 66. Low-resolution EI mass spectra: Finnigan MAT 95, ionizing voltage 70 eV. High-resolution mass spectra: Finnigan MAT 95; preselected ion peak matching at $R \approx 10000$ to be within ± 2 ppm of the exact masses. Elemental analyses: Mikroanalytisches Labor des Instituts für Organische und Biomolekulare Chemie der Universität Göttingen (Germany). Melting points are uncorrected. Solvents for extraction and chromatography were of technical grade and were distilled before use. All reactions were carried out under an atmosphere of dry nitrogen in oven- and/or flame-dried glassware. Benzene, THF, and diethyl ether were distilled from sodium. Dichloromethane was distilled from CaH_2.

General procedure for the preparation of the bicyclo[4.3.0]nonenylstannanes (GP 1): *n*-Butyllithium (2.60 equiv, 2.36 M in hexane) was added at −78 °C to a solution of diisopropylamine (2.60 equiv) in THF, and the mixture was stirred for 30 min. Tri-*n*-butyltin hydride (2.20 equiv) was added to the resulting solution, and stirring was continued for 30 min before copper(I) cyanide (1.10 equiv) was added in one portion. The reaction mixture was warmed to −50 °C until a yellow solution had formed, which was treated with the relevant enol triflate (1.00 equiv) in THF. The resulting solution was warmed to −25 °C and stirred for an additional 2 h. The reaction mixture was poured into pentane and washed with 10% NH_3 solution, water, and brine. After drying over $MgSO_4$ and concentration in vacuo, the residue was taken up in ethyl acetate and the solution, contained in an unsealed vessel, was treated with silver(I) acetate (3.00 equiv) at ambient temperature for 2 h. The reaction mixture was filtered through Celite, washed with water, brine, and dried over $MgSO_4$. After concentration in vacuo, the residue

was purified by column chromatography on neutral aluminum oxide (deactivated with 5% water).

General procedure for [2+2] cycloadditions of dichloroketene (GP 2): Powdered zinc (2.00 equiv) was added to a solution of the relevant halocyclohexadiene (1.00 equiv) in diethyl ether, and the resulting suspension was treated in an ultrasonic bath at 15–20°C for 30 min. Trichloroacetic acid chloride (1.50 equiv) in diethyl ether was then added within 3 h under continuous ultrasonication. The reaction mixture was diluted with diethyl ether and filtered through Celite. The filtrate was washed with sat. $NaHCO_3$ solution and water. After extraction of the combined aqueous phases with diethyl ether, washing of the combined organic layers with brine, drying over $MgSO_4$, and concentration in vacuo, the residue was subjected to column chromatography on silica gel.

General procedure for Stille couplings of bicyclo[4.3.0]nonenylstannanes with 2-bromocyclohexenol triflates (GP 3): A Pyrex bottle containing a magnetic stirring bar was charged with a solution of the relevant enol triflate (1.00 equiv) and the bicyclo[4.3.0]nonenylstannane (1.10–1.30 equiv) in NMP. After purging the solution with argon in an ultrasonic bath for 5 min, $[Pd_2(dba)_3]\cdot CHCl_3$ (2.00–5.00 mol%), LiCl (3.00 equiv), and CuI (2.00–5.00 mol%) were added. Before carefully sealing the bottle with a screw cap, the mixture was purged again with argon in an ultrasonic bath for 5 min. The reaction mixture was stirred vigorously with heating at 90°C for 12 h. After cooling down to ambient temperature, the reaction mixture was poured into diethyl ether and the mixture washed with NH_3 solution (5%) and water. The combined aqueous phases were extracted with diethyl ether, and the combined organic layers were vigorously stirred with sat. KF solution for 45 min. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. If necessary, the residue was adsorbed onto silica gel and purified by column chromatography on silica gel.

General procedure for Diels–Alder reactions of tricyclic dienes (GP 4): A Pyrex bottle, containing a magnetic stirring bar, was charged with a solution of the tricyclic diene and the relevant dienophile in the specified solvent. The resulting solution was purged with argon in an ultrasonic bath for 5 min. The bottle was carefully sealed with a screw cap and, after heating at the specified temperature for the stated time, the volatile components were removed in vacuo, and the residue was purified by column chromatography.

(+)-6-(3*S*,3a*S*,7a*S*)-3-*tert*-Butoxy-3a-methyl-3a,4,5,7a-tetrahydroindanyltri-*n*-butylstannane (*trans*-8): Following GP 1, diisopropylamine (3.69 g, 36.5 mmol) in THF (150 mL) was treated with *n*-butyllithium (15.1 mL, 36.5 mmol, 2.42 M). Tri-*n*-butyltin hydride (8.98 g, 30.9 mmol) and copper(I) cyanide (1.38 g, 15.4 mmol) were added, followed by a solution of the bicyclic enol triflate *trans*-**7** (5.00 g, 14.0 mmol) in THF (15 mL). Workup with pentane (200 mL), 10% NH_3 solution (50 mL), water (2× 50 mL), and brine (40 mL) yielded, after treatment of the crude product with silver(I) acetate (6.50 g, 39.0 mmol) in ethyl acetate (100 mL) and column chromatography on neutral aluminum oxide (100 g, pentane), *trans*-**8** as a colorless oil (5.90 g, 85%). R_f=0.5, pentane/diethyl ether 20:1; IR (film): $\tilde{\nu}$=2976, 2956, 2928, 2872, 2847, 1606, 1461, 1419, 1383, 1359, 1337, 1290, 1251, 1195, 1117, 1070, 1021, 958, 897, 836, 689, 659 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.73 (s, 3H; CH_3), 0.82–1.01 (m, 14H; *n*Bu−CH_3, *n*Bu−CH_2), 1.14 (s, 9H; $C(CH_3)_3$), 1.22–1.40 (m, 7H; *n*Bu−CH_2), 1.42–1.58 (m, 7H; *n*Bu-CH_2), 1.65–1.83 (m, 2H), 1.89–2.16 (m, 2H), 2.20–2.41 (m, 4H), 3.43 (dd, ^3J=6.8, ^3J=8.0 Hz, 1H; 3-H), 5.72 ppm (m_c, 1H; 7-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, add. DEPT): δ= 8.89 (−, 3C, *n*Bu−CH_2), 10.99 (+, CH_3), 13.74 (+, 3C, *n*Bu−CH_3), 24.60 (−, CH_2), 27.40 (−, 3C, *n*Bu−CH_2), 28.72 (+, 3C, $C(CH_3)_3$), 29.24 (−, 3C, *n*Bu−CH_2), 30.77 (−, CH_2), 31.15 (−, CH_2), 35.55 (−, CH_2), 41.51 (C_{quat}, C-3a), 44.75 (+, CH, C-7a), 72.13 (C_{quat}, $C(CH_3)_3$), 79.63 (+, CH, C-3), 138.30 (C_{quat}, C-6), 141.72 ppm (+, CH, C-7); MS (70 eV): *m*/*z* (%): 443/442/441/440/439/438/437 (16/24/100/44/83/33/46) [$M^+-C_4H_9$], 293/292/291/290/289/288/287 (1/1/6/3/5/2/3) [S*n*Bu_3^+], 239/237/236/235/234/233/232/231 (15/12/11/99/32/76/26/42) [S*n*Bu_2H^+], 180/179/178/177/176/175 (11/88/83/53/26/12) [S*n*Bu^+], 135 (5) [$M^+-Sn Bu_3-C_4H_9-CH_3$], 122/121/120/119/118/117 (1/5/26/20/12/10) [SnH^+], 91 (3), 57 (84) [Bu^+], 41 (22); elemental analysis calcd (%) for $C_{26}H_{50}OSn$ (497.37): C 62.78, H 10.13; found C 62.86, H 10.01.

6-(3*S*,3a*S*,7a*R*)-3-*tert*-Butoxy-3a-methyl-3a,4,5,7a-tetrahydroindanyltri-*n*-butylstannane (*cis*-8): Following GP 1, diisopropylamine (1.69 g, 16.5 mmol) in THF (100 mL) was treated with *n*-butyllithium (7.00 mL, 16.5 mmol, 2.36 M). Tri-*n*-butyltin hydride (4.07 g, 14.0 mmol) and copper(I) cyanide (626 mg, 6.99 mmol) were added, followed by bicyclic enol triflate *cis*-**7** (2.26 g, 6.35 mmol) in THF (5 mL). Workup with pentane (100 mL), NH_3 solution (30 mL, 10%), water (2×30 mL), and brine (25 mL) yielded, after treatment of the crude product with silver(I) acetate (3.18 g, 19.1 mmol) in ethyl acetate (80 mL) and column chromatography on neutral aluminum oxide (40 g, pentane), *cis*-**8** as a colorless oil (2.92 g, 92%). R_f=0.5, pentane/diethyl ether 20:1; IR (film): $\tilde{\nu}$=2957, 2925, 2871, 1609, 1464, 1418, 1387, 1376, 1361, 1292, 1198, 1072, 1020, 902, 874, 689 cm^{-1}; ^1H NMR (250 MHz, C_6D_6): δ=0.82–1.04 (m, 15H; *n*Bu−CH_3, *n*Bu−CH_2), 1.13 (s, 3H; CH_3), 1.15 (s, 9H; $C(CH_3)_3$), 1.24–1.79 (m, 16H), 1.89–2.16 (m, 2H), 2.18–2.27 (m, 1H), 2.33 (m_c, 2H), 3.66 (t, ^3J=6.8 Hz, 1H; 3-H), 5.85–5.95 ppm (m, 1H; 7-H); ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ=9.26 (−, 3C, *n*Bu−CH_2), 14.0 (+, 3C, *n*Bu−CH_3), 21.8 (+, CH_3), 27.8 (+, 3C, $C(CH_3)_3$), 28.9 (−, 3C, *n*Bu−CH_2), 29.1 (−, CH_2), 29.3 (−, CH_2), 29.7 (−, 3C, *n*Bu−CH_2), 31.1 (−, CH_2), 32.8 (−, CH_2), 42.2 (C_{quat}, C-3a), 46.2 (+, C-7a), 72.4 (C_{quat}, $C(CH_3)_3$), 76.7 (+, C-3), 137.4 (C_{quat}, C-6), 142.7 ppm (+, C-7); MS (70 eV): *m*/*z* (%): 443/442/441/440/439/438/437 (16/24/100/44/83/33/46) [$M^+-C_4H_9$], 387/386/385/384/383/382/381 (1/2/13/5/16/5/6) [$M^+-C_4H_9-2\times C_4H_8$], 331/330/329/327/326/325/324 (2/1/12/4/11/4/5) [$M^+-C_4H_9-2\times C_4H_8$], 293/292/291/290/289/288/287 (1/1/6/3/5/2/3) [S*n*Bu_3^+], 237/236/235/234/233/232/231 (1/1/4/2/3/2/1) [S*n*Bu_2H^+], 179/178/177/176/175 (2/1/4/1/2) [S*n*BuH^+], 136 (2) [$M^+-Sn Bu_3-C_4H_8-CH_3$], 122/121/120/119/118/117 (1/5/2/4/2/3) [SnH^+], 91 (3), 57 (21) [tBu^+], 41 (3); elemental analysis calcd (%) for $C_{26}H_{50}OSn$ (497.4): C 62.78, H 10.13; found C 62.83, H 10.17.

(2a*S*,4a*S*,7a*S*,7b*R*)-4-Bromo-2,2-dichloro-6,6-dimethyl-2a,4a,7a,7b-tetrahydro-2*H*-5,7-dioxacyclobuta[*e*]inden-1-one (10a): Following GP 2, bromocyclohexadiene **9a** (4.80 g, 20.8 mmol) in diethyl ether (50 mL) was treated with trichloroacetic acid chloride (5.67 g, 31.2 mmol) and powdered zinc (2.72 g, 41.5 mmol). Workup with diethyl ether (100 mL), sat. $NaHCO_3$ solution (50 mL), water (50 mL), extraction with diethyl ether (2×40 mL), and brine (30 mL) provided, after column chromatography (50 g of silica gel, pentane/diethyl ether/triethylamine 1:1:0.01), the product **10a** as a yellow wax (4.45 g, 65%). R_f=0.3; IR (film): $\tilde{\nu}$=2988, 2936, 2881, 1809, 1751, 1648, 1472, 1454, 1382, 1370, 1347, 1306, 1236, 1165, 1072, 1044, 994, 965, 931, 871, 855, 786 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.09 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 2.75 (ddd, ^3J=9.6, ^3J= 4.4, ^3J=1.7 Hz, 1H; 2a-*H*), 3.84 (dd, ^3J=9.6, ^3J=2.5 Hz, 1H; 7b-*H*), 4.02 (d, ^3J=5.7 Hz, 1H; 4a-*H*), 4.19 (dd, ^3J=5.7, ^3J=2.5 Hz, 1H; 7a-*H*), 5.80 ppm (dt, ^3J=4.4, ^3J=1.1 Hz, 1H; 3-*H*); ^{13}C NMR (75.7 MHz, $CDCl_3$ add. APT): δ=26.15 (+, CH_3), 27.57 (+, CH_3), 45.24 (−, CH), 53.35 (−, CH), 70.76 (+, *C*HOC), 72.75 (+, *C*HOC), 87.07 (−, C_{quat}, C-2), 110.16 (−, C_{quat}, C-6), 125.28 (+, CH, C-3), 128.60 (−, C_{quat}, C-4), 190.95 ppm (−, C_{quat}, C-1); MS (70 eV): *m*/*z* (%): 346/344/342/340 (4/27/57/37) [M^+], 331/329/327/325 (4/26/56/35) [M^+-CH_3], 288/286/284/282 (3/20/40/25), 272 (14), 248 (11), 246/244/242/240 (4/26/56/36), 221 (22), 205 (71), 203 (100), 179/177/175/173 (10/53/98/36), 167 (8), 146 (21), 133 (23), 121 (27), 111 (32), 94 (47), 85 (73), 77 (39), 65 (64), 63 (29); elemental analysis calcd (%) for $C_{11}H_{11}BrCl_2O_3$ (342.0): C 40.48, H 3.68; found C 40.24, H 3.66.

(2a*S*,4a*S*,7a*S*,7b*R*)-4-Iodo-2,2-dichloro-6,6-dimethyl-2a,4a,7a,7b-tetrahydro-2*H*-5,7-dioxacyclobuta[*e*]inden-1-one (10b): Following GP 2, the iodocyclohexadiene **9b** (2.50 g, 9.00 mmol) in diethyl ether (25 mL) was treated with powdered zinc (1.18 g, 18.0 mmol) and trichloroacetic acid chloride (2.45 g, 13.5 mmol) in diethyl ether (13 mL). Workup with diethyl ether (100 mL), sat. $NaHCO_3$ solution (50 mL), water (50 mL), and brine (30 mL) yielded, after column chromatography (30 g of silica, pentane/diethyl ether 2:1), product **10b** as a colorless solid (434 mg, 12%). R_f=0.4; ^1H NMR (300 MHz, C_6D_6): δ=1.04 (s, 3H; CH_3), 1.24 (s, 3H; CH_3), 2.61 (ddd, ^3J=9.3, ^3J=4.4, ^3J=1.7 Hz, 1H; 2a-*H*), 3.78 (dd, ^3J= 9.3, ^3J=2.5 Hz, 1H; 7b-*H*), 3.91 (d, ^3J=5.5 Hz, 1H; 4a-*H*), 4.09 (dd, ^3J= 5.5, ^3J=2.5 Hz, 1H; 7a-*H*), 6.03 ppm (dt, ^3J=4.4, ^3J=0.6 Hz, 1H; 3-*H*); ^{13}C NMR (75.6 MHz, $CDCl_3$ add. APT): δ=26.16 (+, CH_3), 27.53 (+, CH_3), 45.79 (+, CH), 52.96 (+, CH), 69.91 (+, *C*HOC), 74.40 (+,

*C*HOC), 90.74 (−, C_{quat}, C-2), 109.84 (−, C_{quat}, C-6), 132.76 (+, CH, C-3), 149.90 (−, C_{quat}, C-4), 204.98 ppm (−, C_{quat}, C-1); MS (70 eV): *m*/*z* (%): 297/295/293/(4/17/26), 265/263/261 (3/15/22/) [M^+−I], 251/249/247 (8/23/33), 209/207/205 (2/9/14), 176 (13), 169 (35), 166/164/162 (25/77/100), 143 (27), 127 (29) [I^+], 125 (56), 111 (17), 99 (28), 95 (55), 85 (32), 77 (53), 66 (41), 61 (15); elemental analysis calcd (%) for $C_{11}H_{11}Cl_2IO_3$ (389.0): C 33.96, H 2.85; found C 34.25, H 2.85.

(3a*R*,5a*R*,8a*R*,8b*S*)-4-Bromo-6,6-dichloro-2,2-dimethyl-3a,5a,6,8,8a,8b-hexahydro-1,3-dioxa[*a*,*s*]indacen-7-one (11): A solution of the bicyclooctenone **10a** (1.99 g, 4.90 mmol) in diethyl ether (40 mL) and methanol (11 mL) was treated with diazomethane in diethyl ether (46 mL, 46 mmol, ca. 1.0 M) added at −15 °C over 45 min. After continued stirring at −15 °C for 15 min, excess diazomethane was quenched with acetic acid. Workup with sat. $NaHCO_3$ solution (2×50 mL), drying over $MgSO_4$, and column chromatography (45 g of silica, pentane/diethyl ether 2:1) yielded the indenone **11** as a yellow wax (1.00 g, 57%). R_f= 0.6; IR (film): $\tilde{\nu}$=2988, 2934, 1771, 1644, 1454, 1404, 1382, 1371, 1322, 1309, 1231, 1170, 1144, 1128, 1070, 1049, 1014, 982, 905, 867, 829, 783 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ=1.21 (s, 3H; CH_3), 1.31 (s, 3H; CH_3), 1.33–1.48 (m, 1H), 1.89 (dd, ^3J=19.5, ^3J=8.2 Hz, 1H; 5a-*H*), 2.70 (m_c, 1H; 8-*H*), 2.97 (m_c, 1H; 8a-*H*), 3.65 (t, ^3J=4.9 Hz, 1H; 8b-*H*), 3.93 (dd, ^3J=4.9, ^3J=2.2 Hz, 1H; 3a-*H*), 6.07 ppm (d, ^3J=2.7 Hz, 1H; 5-*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$ add. APT): δ=26.65 (+, CH_3), 27.82 (+, CH_3), 32.30 (+, CH), 32.89 (−, CH_2), 50.61 (+, CH), 74.00 (+, *C*HOC), 74.58 (+, *C*HOC), 87.05 (−, C_{quat}, C-6), 110.24 (−, C_{quat}, C-2), 125.44 (+, CH, C-5), 127.60 (−, C_{quat}, C-4), 197.34 ppm (−, C_{quat}, C-8); MS (70 eV): *m*/*z* (%): 345/343/341/339 (10/64/100/79) [M^+−CH_3], 305 (3) 299 (9), 270 (7), 263 (15), 243/241/239/237 (22/22/45/30), 217 (13), 212 (4), 191 (7), 184 (12), 182 (15), 172 (10), 161 (7), 133 (10), 127 (17), 125 (35), 112 (12), 101 (8), 89 (23), 75 (13), 65 (17), 61 (25); HRMS: *m*/*z*: calcd for $C_{12}H_{13}BrCl_2O_3$−CH_3 (341.0): 340.9160 (correct HRMS).

(3a*R*,5a*R*,8a*R*,8b*S*)-4-Bromo-2,2-dimethyl-3a,5a,6,8,8a,8b-hexahydro-1,3-dioxa[*a*,*s*]indacene-7-one (12): Powdered zinc (660 mg, 10.1 mmol) was added to a solution of acetic acid (586 mg, 9.75 mmol) and tetramethylethylenediamine (992 mg, 8.53 mmol) in ethanol (6.0 mL), and the mixture was stirred at 23 °C for 20 min. After addition of the dichloroindenone **11** (620 mg, 1.74 mmol) in ethanol (3.0 mL), the mixture was stirred at 23 °C for 3 h. The reaction mixture was poured into diethyl ether (75 mL), and the solution was filtered through Celite. The filtrate was washed with water (30 mL) and sat. $NaHCO_3$ solution (25 mL). After extraction of the combined aqueous phases with diethyl ether (2× 50 mL), the combined organic layers were dried over $MgSO_4$. After concentration in vacuo, the residue was purified by column chromatography (35 g of silica, pentane/diethyl ether 2:1) to yield the hexahydroindenone **12** as a yellow oil (415 mg, 83%). R_f=0.5; ^1H NMR (300 MHz, C_6D_6): δ=1.26 (s, 3H; CH_3), 1.36 (s, 3H; CH_3), 1.42–1.58 (m, 1H), 1.66–1.82 (m, 3H), 2.30 (m_c, 1H; 5a-*H*), 2.49 (m_c, 1H; 8a-*H*), 3.83 (dd, ^3J=4.9, ^3J= 3.6 Hz, 1H; 8b-*H*), 4.11 (dd, ^3J=5.2, ^3J=2.2 Hz, 1H; 3a-*H*), 5.46 ppm (d, ^3J=2.7 Hz, 1H; 5-*H*); ^{13}C NMR (75.6 MHz, $CDCl_3$ add. APT): δ=26.77 (+, CH_3), 27.89 (+, CH_3), 35.15 (+, CH), 36.34 (−, CH_2), 38.27 (−, CH_2), 44.27 (+, CH), 74.11 (+, *C*HOC), 75.54 (+, *C*HOC), 109.68 (−, C_{quat}, C-2), 123.96 (−, C_{quat}, C-4), 132.55 (+, CH, C-5), 213.07 ppm (−; C_{quat}, C-8); MS (70 eV): *m*/*z* (%): 288/286 (12/13) [M^+], 273/271 (100/99) [M^+−CH_3], 231/229 (56/61) [M^+−$C(CH_3)_2$], 213/211 (35/37) [M^+ −$HOCH(CH_3)_2$], 189 (7), 186 (12), 185/183 (32/28), 171/169 (42/43), 159 (5), 150 (7), 149 (20), 132 (27), 121 (14), 107 (25), 104 (32), 91 (42), 77 (47), 65 (39), 59 (13); HRMS: *m*/*z*: calcd for $C_{12}H_{15}BrO_3$ (287.1): 286.0204 (correct HRMS).

(3a*R*,5a*R*,8a*R*,8b*S*)-4-Bromo-2,2-dimethyl-spiro(1′,3′-dioxolane[2′,7]-3a,5a,6,8,8a,8b-hexahydro-1,3-dioxa[*a*,*s*]indacene (13): A solution of the hexahydroindenone **12** (1.10 g, 3.83 mmol), ethylene glycol (1.34 g, 21.6 mmol), and triethyl orthoformate (1.30 g, 8.78 mmol) in dichloromethane (40.0 mL) was treated with *p*-toluenesulfonic acid (10.0 mg, 0.160 mmol) at 23 °C for 23 h. After this time, the reaction mixture was poured into diethyl ether (50 mL) and the mixture washed with sat. $NaHCO_3$ solution (20 mL) and water (20 mL). After extraction of the combined aqueous phases with diethyl ether (2×35 mL), the combined organic layers were dried over $MgSO_4$. Concentration in vacuo and column chromatography (40 g of silica, pentane/diethyl ether 2:1) yielded compound **13** as a colorless oil (821 mg, 65%). R_f=0.4; ^1H NMR (300 MHz, C_6D_6): δ=1.30 (s, 3H; CH_3), 1.47 (s, 3H; CH_3), 1.49–1.75 (m, 3H), 1.92 (dd, ^3J=14.2, ^3J=8.0 Hz, 1H), 2.50–2.69 (m, 2H), 3.32–3.52 (m, 4H; 2′-*H*, 3′-*H*), 3.99 (dd, ^3J=5.2, ^3J=3.3 Hz, 1H; 8b-*H*), 4.25 (dd, ^3J=5.2, ^3J=1.7 Hz, 1H; 3a-*H*), 5.76 ppm (d, ^3J=2.7 Hz, 1H; 5-*H*); ^{13}C NMR (75.6 MHz, $CDCl_3$ add. APT): δ=27.04 (+, CH_3), 28.21 (+, CH_3), 36.59 (+, CH), 38.15 (+, CH), 38.15 (−, CH_2), 42.38 (−, CH_2), 63.87 (−, CH_2O), 64.46 (−, CH_2O), 74.79 (+, CHOC), 76.15 (+, CHOC), 109.08 (−, C_{quat}, C-2), 116.48 (−, C_{quat}, C-7), 121.94 (−, C_{quat}, C-4), 134.21 ppm (+, CH, C-5); MS (70 eV): *m*/*z* (%): 332/330 (5/6) [M^+], 317/315 (58/59) [M^+−CH_3], 275/273 (13/14), 257/253 (10/9), 231/229 (12/12), 213/211 (10/10), 193 (30), 169 (10), 165 (8), 137 (5), 132 (12), 128 (55), 87 (82), 86 (100), 77 (26), 65 (22), 55 (10), 52 (6); HRMS: *m*/*z*: calcd for $C_{14}H_{19}BrO_4$ (331.2): 332.0445 (correct HRMS).

(3a*R*,5a*R*,8a*R*,8b*S*)-Tributyl{spiro[1′,3′-dioxolane[2′,7]-(2,2-dimethyl-5a,6,7,8,8a,8b-hexahydro-3a*H*-1′,4′-dioxaspiro[4′.7]-1,3-dioxa-[*a*,*s*]indacene-4-yl)]}stannane (14): *tert*-Butyllithium (3.59 mL, 5.38 mmol 1.50 M in hexane) was added dropwise to a solution of bicyclononenylbromide **13** (810 g, 2.54 mmol) in THF (30 mL) at −78 °C, and the mixture was stirred for 1 h. The reaction mixture was warmed to 0 °C and stirred for 30 min at this temperature. After cooling to −78 °C, tri-*n*-butyltin chloride (1.19 g, 3.67 mmol) was added dropwise, and the reaction mixture was warmed to 0 °C within 4 h. The reaction mixture was then poured into diethyl ether (100 mL) and washed with NH_4Cl solution (35 mL, 1.0 M). After drying over $MgSO_4$, concentration in vacuo, and column chromatography (35 g of silica, pentane/diethyl ether 2:1), the bicyclo[4.3.0]nonenylstannane **14** was obtained as a colorless oil (923 mg, 70%). R_f=0.7; IR (film): $\tilde{\nu}$=2956, 2927, 2871, 1614, 1463, 1430, 1376, 1366, 1333, 1312, 1293, 1221, 1147, 1104, 1069, 1044, 960, 945, 905, 874, 788 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ=0.98 (t, ^3J=7.2 Hz, 9H; *n*BuSn) 1.39 (s, 3H; CH_3), 1.40–1.48 (m, 9H; *n*BuSn), 1.50 (s, 3H; CH_3), 1.63–1.93 (m, 12H), 2.18 (dd, ^3J=13.7, ^3J=8.8 Hz, 1H), 2.67–2.83 (m, 2H), 3.36–3.51 (m, 4H; 2′-*H*, 3′-*H*), 4.20 (dd, ^3J=5.2, ^3J=3.3 Hz, 1H; 8b-*H*), 4.47 (dt, ^3J=5.2, ^3J=1.1 Hz, 1H; 3a-*H*), 5.75 ppm (d, ^3J=1.4 Hz, 1H; 5-*H*); ^{13}C NMR (75.6 MHz, $CDCl_3$ add. APT): δ=9.88 (+, CH_3, 3C, *n*BuSn), 13.93 (−, CH_2, 3C, *n*BuSn), 27.72 (−, CH_2, 3C, *n*BuSn), 28.12 (+, CH_3), 28.57 (+, CH_3), 29.43 (−, CH_2, 3C, *n*BuSn), 35.19 (+, CH), 38.55 (+, CH), 38.89 (−, CH_2), 43.56 (−, CH_2), 63.81 (−, CH_2, CH_2O), 64.32 (−, CH_2, CH_2O), 74.52 (+, CHOC), 74.86 (+, CHOC), 108.26 (−, C_{quat}, C-2), 116.86 (−, C_{quat}, C-7), 138.84 (−, C_{quat}, C-4), 141.36 ppm (+, CH, C-5); MS (70 eV): *m*/*z* (%): 530/529/528/527/526/525/524 (6/16/12/28/12/18) [M^+−CH_3], 487/486/485/484/483/482/481 (20/28/100/52/84/30/52), 429/428/427/426/425/424/423 (15/21/88/40/61/30/34), 385/384/383/382/381/380/379 (4/4/17/10/21/8/12), 339 (2), 327 (5), 291 (4), 270/269/268/267/266/265/264 (6/5/26/10/22/7/12), 252 (6), 235 (5), 212 (10), 178/177/176/175/174/173/172 (20/5/23/6/17/4/5), 160 (1), 133 (11), 119 (6), 105 (10), 91 (21), 87 (14), 77 (7), 59 (2); elemental analysis calcd (%) for $C_{26}H_{46}O_4Sn$ (541.2): C 57.69, H 8.56; found C 57.32, H 8.68.

(2a*S*,4a*S*,7a*S*,7b*R*)-4-Bromo-2-chloro-6,6-dimethyl-2a,4a,7a,7b-tetrahydro-2*H*-5,7-dioxacyclobuta[*e*]inden-1-one (15): A solution of the dichlorobicyclooctene **11** (0.500 g, 1.53 mmol) in methanol (1.20 mL) and THF (5.00 mL) was treated with powdered zinc (401 mg, 6.13 mmol) and NH_4Cl (328 mg, 6.13 mmol) at 23 °C for 2 h in an ultrasonic bath. After this time, the reaction mixture was poured into diethyl ether (75 mL), and the solution was filtered through Celite. The filtrate was washed with water (30 mL) and brine (25 mL). After drying over $MgSO_4$ and concentration in vacuo, column chromatography (30 g of silica, pentane/diethyl ether 1:1) yielded the product **15** as a colorless wax (83.1 mg, 18%). R_f= 0.6; ^1H NMR (300 MHz, $CDCl_3$): δ=1.13 (s, 3H; CH_3), 1.34 (s, 3H; CH_3), 2.47 (m_c, 1H; 2a-*H*), 3.19 (m_c, 1H; 2-*H*), 3.93 (m_C, 1H; 7b-*H*), 4.21–4.28 (m, 1H; 7a-*H*), 4.33 (dd, ^3J=5.8, ^3J=2.7 Hz, 1H; 4a-*H*), 5.97 ppm (dt, ^3J=4.1, ^3J=0.83 Hz, 1H; 3-*H*); ^{13}C NMR (75.5.9 MHz, $CDCl_3$ add. APT): δ=26.25 (+, CH_3), 27.55 (+, CH_3), 31.79 (−, CH), 53.14 (−, CH), 63.77 (+, CH, C-2), 71.03 (+, *C*HOC), 73.20 (+, *C*HOC), 109.95 (−, C_{quat}, C-6), 125.90 (+, CH, C-3), 127.34 (−, C_{quat}, C-4), 196.16 ppm (−, C_{quat}, C-1); MS (70 eV): *m*/*z* (%): 310/308/306 (2/7/5) [M^+], 295/293/291 (7/25/20) [M^+−CH_3], 252/250/248 (5/19/15), 240/238/236 (31/100/85), 221 (8), 217 (26), 215 (28), 185 (20), 173 (98), 169 (63),

159 (30), 141 (39), 129 (33), 112 (16), 101 (44), 99 (98), 94 (71), 89 (21), 77 (96), 65 (67), 63 (39), 59 (31).

1,4-Dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (17): Sodium bis(trimethylsilyl)amide solution (13.4 mL, 26.8 mmol, 2.00 M in THF) was added to a solution of 1,4-dioxaspiro[4.5]decan-8-one (4.00 g, 25.6 mmol) in diethyl ether (300 mL) at −20 °C. After 60 min at this temperature, the solution was treated with trifluoromethanesulfonic acid anhydride (4.52 mL, 26.9 mmol). After stirring for 16 h, during which time the temperature was raised to 22 °C, the reaction mixture was washed with sat. $NaHCO_3$ solution (50 mL) and water (50 mL). The aqueous phases were re-extracted with diethyl ether (2×50 mL), and the combined organic phases were dried over $MgSO_4$. After removal of the volatile components in vacuo, the residue was purified by column chromatography on silica gel (25 g, pentane/diethyl ether 5:1) to yield the title compound **17** (R_f=0.4) as a colorless oil (7.08 g, 96 %), the analytical data for which were consistent with those reported previously.[15]

(1′*S*,3a′*S*,7a′*S*)-8-(1′-*tert*-Butoxy-7a′-methyl-2′,3′,3a′,6′,7′,7a′-hexahydro-1′*H*-inden-5′-yl)-1,4-dioxaspiro[4.5]dec-7-ene (*trans*-19): Following GP 3, enol triflate **17** (288 mg, 1.00 mmol) and bicyclo[4.3.0]nonenylstannane *trans*-**8** (597 mg, 1.20 mmol) in NMP (5 mL) were treated with [Pd_2(dba)$_3$]·$CHCl_3$ (54.0 mg, 52.2 μmol), LiCl (127 mg, 3.00 mmol), and CuI (30.0 mg, 158 μmol). Workup with diethyl ether (50 mL), water (2× 25 mL), extraction with diethyl ether (2×30 mL), treatment with sat. KF solution (30 mL), and column chromatography (27 g of silica gel, pentane/diethyl ether 10:1) yielded the tricyclic butadiene *trans*-**19** as a colorless wax (265 mg, 77 %). R_f=0.4; IR (film): $\tilde{\nu}$=2975, 2930, 2873, 1465, 1457, 1388, 1377, 1362, 1341, 1252, 1197, 1165, 1118, 1059, 1015, 982, 946, 907, 859, 734, 701 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.69 (s, 3H; CH_3), 1.17 (s, 9H; $C(CH_3)_3$), 1.22–1.62 (m, 3H), 1.75–2.21 (m, 6H), 2.24–2.33 (m, 6H), 3.49 (dd, ^3J=11.4, ^3J=8.0 Hz, 1H; 1′-*H*), 3.98 (s, 4H; 2-*H*, 3-*H*), 5.22–5.76 ppm (m, 2H; 4′-*H*, 7-*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$, add. APT): δ=10.95 (+, CH_3), 24.46 (−, CH_2), 24.77 (−, 2C, CH_2), 28.68 (+, 3C, $C(CH_3)_3$), 31.18 (−, CH_2), 31.70 (−, CH_2), 34.15 (−, CH_2), 35.96 (−, CH_2), 41.96 (−, C_{quat}, C-7a′), 44.36 (+, CH, C-3′), 64.35 (−, OCH_2CH_2O), 64.40 (−, OCH_2CH_2O), 72.17 (−, C_{quat}, $C(CH_3)_3$), 79.35 (+, CH, C-1′), 108.02 (−, C_{quat}, C-5), 118.51 (−, C_{quat}), 123.81 (−, C_{quat}), 135.29 (−, C_{quat}), 135.82 ppm (−, C_{quat}); MS (70 eV): *m*/*z* (%): 346 (10) [M^+], 316 (1), 290 (100) [$M^+-C_4H_8$], 289 (55) [$M^+-C_4H_9$], 272 (5), 228 (26), 203 (22), 185 (10), 171 (6), 159 (9), 131 (12), 105 (11), 91 (10), 86 (22), 79 (4), 57 (38) [$C_4H_9^+$], 41 (9); HRMS: *m*/*z*: calcd for $C_{22}H_{34}O_3$+H^+ (347.5): 347.25814 (correct HRMS).

(1′*S*,3a′*R*,7a′*S*)-8-(1′-*tert*-Butoxy-7a′-methyl-2′,3′,3a′,6′,7′,7a′-hexahydro-1′*H*-inden-5′-yl)-1,4-dioxaspiro[4.5]dec-7-ene (*cis*-19): Following GP 3, enol triflate **17** (288 mg, 1.00 mmol) and bicyclo[4.3.0]nonenylstannane *cis*-**8** (599 mg, 1.20 mmol) in NMP (5 mL) were treated with [Pd_2(dba)$_3$]·$CHCl_3$ (54.1 mg, 52.2 μmol), LiCl (127 mg, 3.00 mmol) and CuI (30.0 mg, 158 μmol). Workup with diethyl ether (45 mL), water (2× 25 mL), extraction with diethyl ether (2×30 mL), treatment with sat. KF solution (30 mL), and column chromatography (25 g of silica gel, pentane/diethyl ether 10:1) yielded the tricyclic butadiene *cis*-**19** as a colorless wax (253 mg, 73 %). R_f=0.4; IR (film): $\tilde{\nu}$=2971, 2929, 2873, 1621, 1493, 1463, 1447, 1433, 1422, 1387, 1362, 1303, 1255, 1224, 1198, 1140, 1117, 1061, 1058, 1040, 1017, 994, 950, 897, 875, 861 cm^{-1}; ^1H NMR (250 MHz, C_6D_6): δ=1.15 (s, 9H, $C(CH_3)_3$), 1.17 (s, 3H, CH_3), 1.21–1.48 (m, 2H), 1.58–1.78 (m, 3H), 1.87 (m_c, 2H), 1.93–2.20 (m, 3H), 2.23 (m_c, 4H), 2.24–2.33 (m, 1H), 3.53–3.62 (m, 5H, 1′-*H*, 2-*H*, 3-*H*), 5.69 (m_c, 1H, 7′-*H*), 5.39 ppm (m_c, 1H, 4′-H); ^{13}C NMR (75.5 MHz, $CDCl_3$ add. APT): δ=21.51 (+, CH_3), 22.79 (−, CH_2), 25.37 (−, CH_2), 28.82 (+, 3C, C-$(CH_3)_3$), 29.36 (−, CH_2), 30.90 (−, CH_2), 31.84 (−, CH_2), 33.12 (−, CH_2), 36.62 (−, CH_2), 42.15 (−, C_{quat}, C-7a′), 44.92 (+, CH, C-3a′), 64.28 (−, CH_2, 2C, OCH_2CH_2O), 72.36 (−, C_{quat}, $C(CH_3)_3$), 76.86 (+, CH, C-1′), 108.22 (−, C_{quat}, C-5), 119.23 (+, CH), 126.76 (+, CH), 133.88 (−, C_{quat}), 136.43 ppm (−, C_{quat}); MS (70 eV): *m*/*z* (%): 346 (3) [M^+], 321 (1), 306 (3), 290 (100) [$M^+-C_4H_8$], 289 (46) [$M^+-C_4H_9$], 245 (4), 228 (30), 203 (9), 185 (9), 159 (11), 145 (13), 131 (20), 97 (19), 91 (22), 86 (42), 79 (10), 57 (88) [$C_4H_9^+$], 41 (26); ESI-HRMS: calcd for $C_{22}H_{34}O_3$+H^+ (347.5): 347.25807 (correct HRMS).

(3a*R*,5a*R*,8a*R*,8b*S*)-4′-Cyclohex-1-enyl-2,2-dimethyl-spiro(1′,3′-dioxolane[2′,7]-3a,5a,6,8,8a,8b-hexahydro-1,3-dioxa[*a*,*s*]indacene) (20): Following GP 3, a solution of the enol triflate **18** (348 mg, 1.48 mmol) and the bicyclo[4.3.0]nonenylstannane **14** (400 mg, 0.739 mmol) in NMP (7.0 mL) was treated with [Pd_2(dba)$_3$]·$CHCl_3$ (81.7 mg, 78.9 μmol), LiCl (188 mg, 4.43 mmol), and CuI (281 mg, 1.88 mmol) at 65 °C for 13 h. Workup with diethyl ether (80 mL) and water (2×25 mL), extraction with diethyl ether (2×40 mL), treatment with sat. KF solution (35 mL), and column chromatography (22 g of silica gel, pentane/diethyl ether 2:1) yielded the tricyclic butadiene **20** as a colorless oil (84.0 mg, 34 %). R_f= 0.3; IR (film): $\tilde{\nu}$=2972, 2934, 2873, 1462, 1453, 1382, 1352, 1250, 1184, 1052, 1010, 981, 936, 858, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.33 (s, 3H; CH_3), 1.40 (s, 3H; CH_3), 1.69–1.81 (m, 4H), 1.85–1.97 (m, 2H), 2.00–2.22 (m, 5H), 2.52–2.84 (m, 3H), 3.33–3.57 (m, 4H; 2″-*H*, 3″-*H*), 4.21 (t, ^3J=6.1 Hz, 1H; 8a-*H*), 4.61 (d, ^3J=5.2 Hz, 1H; 3a-*H*), 5.57 (d, ^3J=3.3 Hz, 1H; 5-*H*), 6.23 ppm (m_c, 1H; 2′-H); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ=22.82 (−, CH_2), 24.61 (−, CH_2), 26.99 (+, CH_3), 28.43 (+, CH_3), 33.92 (−, CH_2), 34.03 (+, CH), 36.73 (−, CH_2), 38.45 (−, CH_2), 39.23 (+, CH), 43.58 (−, CH_2), 63.85 (−, OCH_2CH_2O), 64.46 (−, OCH_2CH_2O), 72.11 (+, CH, *C*HOC), 74.83 (+, CH, *C*HOC), 108.61 (−, C_{quat}, C-2), 116.98 (−, C_{quat}, C-7), 119.90 (+, CH, C-2′), 130.82 (+, CH, C-5), 137.83 (−, C_{quat}), 137.83 ppm (−, C_{quat}); MS (70 eV): *m*/*z* (%): 332 (10) [M^+], 317 (14) [M^+-CH_3], 309 (27), 292 (31), 273 (100), 258 (11), 229 (34), 201 (28), 189 (19), 167 (8), 141 (17), 126 (22), 99 (15), 91 (21), 87 (41), 83 (33), 73 (10), 67 (17); HRMS: *m*/*z*: calcd for $C_{20}H_{28}O_4$ (332.4): 332.1987 (correct HRMS).

(3a*R*,3b*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-*tert*-Butoxy-9a-methyl-spiro(1′,3′dioxolane[2′,5]-3b,4,5,6,7,8,9,9a,10,11,12,12a,12b,12c-tetradecahydro-3a*H*-2-oxadicyclopenta[*a*,*l*]phenanthrene-1,3-dione) (*trans*-21): Following GP 4, a solution of the tricyclic diene *trans*-**19** (100 mg, 0.289 mmol) and maleic anhydride (35.4 mg, 0.361 mmol) in benzene (2.0 mL) was stirred at ambient temperature for 12 h. Column chromatography (32 g of silica gel, diethyl ether/pentane 1:1) provided the title product *trans*-**21** as a colorless wax (103 mg, 80 %). R_f=0.4; $[\alpha]_D^{20}$=−13.5 (c=1.23 in MeOAc); IR (film): $\tilde{\nu}$=2973, 2882, 1717, 1700, 1653, 1635, 1557, 1506, 1447, 1417, 1388, 1363, 1288, 1238, 1197, 1118, 1092, 1060, 946, 910, 734 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ=0.64 (s, 3H; CH_3), 1.07 (s, 9H; $C(CH_3)_3$), 1.58–1.73 (m, 5H), 1.82–2.19 (m, 10H), 2.21–2.38 (m, 3H), 2.68 (t, ^3J=17.5 Hz, 1H), 3.34 (t, ^3J=7.2 Hz, 1H; 17-H), 3.43–3.60 ppm (m, 4H; OCH_2CH_2O); ^{13}C NMR (75.5 MHz, C_6D_6, add. APT): δ=11.06 (+, CH_3), 23.78 (−, CH_2), 24.87 (−, CH_2), 25.10 (−, CH_2), 28.92 (+, 3C, $C(CH_3)_3$), 31.54 (−, CH_2), 33.53 (−, CH_2), 33.71 (+, CH), 34.17 (−, CH_2), 34.90 (−, CH_2), 39.29 (+, CH), 42.00 (+, CH), 42.77 (−, C_{quat}, C-13), 43.04 (+, CH), 44.91 (+, CH), 64.26 (−, 2C, OCH_2CH_2O), 72.32 (−, C_{quat}, $C(CH_3)_3$), 80.44 (+, CH, C-17), 109.43 (−, C_{quat}, C-5), 130.38 (−, C_{quat}, C=C), 131.80 (−, C_{quat}, C=C), 171.85 (−, C_{quat}, OC=O), 172.21 ppm (−, C_{quat}, OC=O); MS (70 eV): *m*/*z* (%): 444 (18) [M^+], 416 (59), 388 (76) [$M^+-C_4H_8$], 360 (100), 342 (30), 315 (15), 297 (56), 286 (10), 253 (12), 203 (7), 169 (6), 155 (11), 131 (15), 99 (41), 86 (64), 57 (100) [$C_4H_9^+$], 41 (24); HRMS: *m*/*z*: calcd for $C_{26}H_{36}O_6$+H^+ (445.6): 445.25847 (correct HRMS); the X-ray crystal structure analysis of *trans*-**21** has been published elsewhere.[23]

(6*S*,7*S*,5*R*,8*S*,13*R*,14*S*,17*S*)-17-*tert*-Butoxy-13-methyl-spiro(1′,3′-dioxolane[2′,3]-2,3,4,5,6,7,8,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-6,7-dicarbonitrile) (*trans*-22): Following GP 4, a solution of the tricyclic diene *trans*-**19** (350 mg, 1.01 mmol) and fumaronitrile (117 mg, 1.50 mmol) in toluene (2.00 mL) was heated at 110 °C for 16 h. Column chromatography (25 g of silica gel, pentane/diethyl ether 1:1) provided the title compound *trans*-**22** (357 mg, 84 %) as colorless crystals. Crystals suitable for X-ray diffraction were grown from pentane/diethyl ether 1:1 by slow evaporation of the solvent. M.p.: 183–184 °C; R_f=0.4; $[\alpha]_D^{20}$=+36.5 (c=1.06 in MeOAc); IR (film): $\tilde{\nu}$=2973, 2931, 2882, 2296, 1700, 1653, 1635, 1472, 1457, 1394, 1362, 1246, 1196, 1143, 1107, 1094, 1068, 1041, 1017, 982, 946, 906, 881 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ=0.86 (s, 3H; CH_3), 1.16 (s, 9H; $C(CH_3)_3$), 1.32–2.13 (m, 13H), 2.29 (m_c, 1H), 2.55 (m_c, 1H), 2.71–2.86 (m, 2H), 3.00–3.14 (m, 2H), 3.46 (t, ^3J=8.3 Hz, 1H; 17-H), 3.98 ppm (m_c, 4H; OCH_2CH_2O); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ=10.77 (+, CH_3), 23.62 (−, CH_2), 24.13 (−, CH_2), 26.78 (−, CH_2), 28.67 (+, 3C, $C(CH_3)_3$), 29.53 (+,

CH), 30.89 (−, CH_2), 31.89 (+, CH_2), 35.44 (−, CH_2), 36.12 (+, CH), 36.12 (−, CH_2), 37.62 (+, CH), 42.54 (−, CH_2), 42.64 (−, CH_2), 47.13 (+, CH), 64.46 (−, OCH_2CH_2O), 64.57 (−, OCH_2CH_2O), 72.54 (−, C_{quat}, $C(CH_3)_3$), 80.01 (+, CH, C-17), 108.12 (−, C_{quat}, OCO), 118.33 (−, C_{quat}, CN), 119.37 (−, C_{quat}, CN), 127.54 (−, C_{quat}), 128.06 ppm (−, C_{quat}); MS (70 eV): *m/z* (%): 424 (29) [M^+], 396 (6), 368 (51), 350 (31), 323 (26), 305 (14), 279 (42), 262 (14), 235 (6), 194 (2), 180 (8), 168 (4), 129 (4), 99 (10), 86 (56), 57 (100) [$C_4H_9^+$], 41 (14); HRMS: *m/z*: calcd for $C_{26}H_{36}O_3N_2+H^+$ (425.6): 425.280358 (correct HRMS); the X-ray crystal structure analysis of *trans*-**22** has previously been published.[23]

(3a*R*,3b*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-*tert*-Butoxy-2,9a-dimethyl-spiro(1′,3′-dioxolane[2′,5]-3b,6,7,8,9,9a,10,11,12,12a,12b,12c-dodecahydro-3a*H*,4*H*-2-azadicyclopenta[*a*,*l*]phenanthrene-1,3-dione) (*trans*-23): Following GP 4, a solution of the tricyclic diene *trans*-**19** (80.4 mg, 0.232 mmol) in benzene (1.00 mL) and *N*-methylmaleimide (42.9 mg, 0.348 mmol) was heated at 90 °C for 15 h. Column chromatography (15 g of silica, pentane/diethyl ether/methanol 1:1:0.04) provided the title compound *trans*-**23** as a colorless wax (83.9 mg, 79 %). R_f = 0.3; IR (film): $\tilde{\nu}$ = 2974, 2936, 2874, 1718, 1653, 1457, 1437, 1391, 1368, 1249, 1196, 1153, 1048, 957, 903, 845, 754 cm^{-1}; ^1H NMR (250 MHz, C_6D_6): δ = 0.78 (s, 3H; CH_3), 0.80–1.00 (m, 2H), 1.09 (s, 9H; $C(CH_3)_3$), 1.13–1.38 (m, 3H), 1.52–1.79 (m, 3H), 1.82–2.27 (m, 4H), 2.30–2.58 (m, 6H), 2.61 (s, 3H; NCH_3), 2.99 (t, ^3J = 13.6 Hz, 1H), 3.39 (t, ^3J = 8.3 Hz, 1H; 10-H), 3.52–3.68 ppm (m, 4H; OCH_2CH_2O); ^{13}C NMR (62.9 MHz, C_6D_6, add. DEPT): δ = 11.30 (+, CH_3), 23.86 (−, CH_2), 24.28 (−, CH_2), 24.77 (+, CH), 25.31 (−, CH_2), 28.86 (+, CH, 3C, $C(CH_3)_3$), 31.69 (−, CH_2), 33.90 (−, CH_2), 34.47 (+, CH), 34.47 (−, CH_2), 40.36 (−, CH_2), 41.55 (+, CH), 42.25 (+, CH), 42.78 (+, CH), 42.82 (C_{quat}, C-9a), 43.99 (+, CH), 64.12 (−, 2C, OCH_2CH_2O), 72.16 (C_{quat}, $C(CH_3)_3$), 80.79 (+, CH, C-10), 109.99 (C_{quat}, C-5), 130.09 (C_{quat}), 131.43 (C_{quat}), 177.43 (C_{quat}, NC=O), 177.67 ppm (C_{quat}, NC=O); MS (70 eV): *m/z* (%): 457 (2) [M^+], 401 (20) [$M^+-C_4H_8$], 400 (6) [$M^+-C_4H_9$], 356 (2), 339 (8), 289 (2), 227 (1), 155 (1), 112 (2), 99 (7), 78 (100), 52 (10), 45 (5); HRMS: *m/z*: calcd for $C_{27}H_{39}O_5N+H^+$ (458.6): 458.29005 (correct HRMS).

Dimethyl(5*R*,8*S*,13*S*,14*S*,17*S*)-17-*tert*-butoxy-13-methyl-spiro(1′,3′dioxolane[2′,3]-2,3,4,5,8,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthrene-6,7-dicarboxylate) (*trans*-24): Following GP 4, a solution of the tricyclic diene *trans*-**19** (100 mg, 0.289 mmol) and dimethyl acetylenedicarboxylate (103 mg, 0.726 mmol) in benzene (1.00 mL) was heated at 90 °C for 14 h. Column chromatography (30 g of silica gel, pentane/diethyl ether 1:1) provided the title product *trans*-**24** as a colorless wax (91.8 mg, 65 %). R_f = 0.4; $[\alpha]_D^{20}$ = +79.5 (*c* = 1.17 in MeOAc); IR (film): $\tilde{\nu}$ = 2972, 2845, 1739, 1652, 1635, 1464, 1419, 1387, 1374, 1250, 1224, 1191, 1109, 1090, 1014, 923, 858 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (s, 3H; CH_3), 1.09 (s, 9H; $C(CH_3)_3$), 1.13–1.60 (m, 3H), 1.65–1.99 (m, 5H), 2.42–2.76 (m, 7H), 3.00–3.11 (m, 1H), 3.19–3.25 (m, 1H), 3.31 (dd, ^3J = 8.7, ^3J = 6.3 Hz, 1H; 17-*H*), 3.72 (s, 3H; OCH_3), 3.77 (s, 3H; OCH_3), 3.91–4.05 ppm (m, 4H; OCH_2CH_2O); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): δ = 11.68 (+, CH_3), 23.35 (−, CH_2), 24.75 (−, CH_2), 26.12 (−, CH_2), 28.66 (+, 3C, $C(CH_3)_3$), 31.26 (−, CH_2), 37.41 (−, CH_2), 38.65 (+, CH), 39.32 (−, CH_2), 40.26 (+, CH), 43.81 (−, CH_2), 44.10 (−, C_{quat}, C-13), 51.98 (+, CH), 52.09 (+, CH), 54.41 (+, CH), 64.37 (−, OCH_2CH_2O), 64.39 (−, OCH_2CH_2O), 72.36 (−, C_{quat}, $C(CH_3)_3$), 79.56 (+, CH, C-17), 108.13 (−, C_{quat}, C-3), 126.31 (−, C_{quat}), 130.80 (−, C_{quat}), 135.56 (−, C_{quat}), 149.03 (−, C_{quat}), 168.44 (−, C_{quat}, C=O), 169.01 ppm (−, C_{quat}, C=O); MS (70 eV): *m/z* (%): 488 (6) [M^+], 456 (100), 428 (3), 399 (54), 341 (6), 301 (5), 288 (9), 275 (12), 230 (4), 203 (1), 143 (2), 115 (4), 99 (15), 86 (12), 57 (52) [$C_4H_9^+$], 41 (12); HRMS: *m/z*: calcd for $C_{28}H_{40}O_7+H^+$ (489.6): 489.28468 (correct HRMS).

(5*R*,8*S*,13*S*,14*S*,17*S*)-Spiro(1′,3′-dioxolane-[2′,3]-17-*tert*-butoxy-6-chloro-13-methyl-2,3,4,5,6,7,8,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthrene-6-carbonitrile) (*trans*-25): Following GP 4, the tricyclic diene (*trans*-**19**) (100 mg, 0.289 mmol) and 2-chloroacrylonitrile (0.200 mL) in benzene (1.0 mL) were heated at 90 °C for 14 h. Column chromatography (35 g of silica gel, pentane/diethyl ether 3:1) provided the title compound *trans*-**25** as a mixture of isomers and as a colorless wax (84.0 mg, 67 %). R_f = 0.4; IR (film): $\tilde{\nu}$ = 2973, 2931, 1717, 1675, 1635, 1617, 1472, 1457, 1437, 1419, 1389, 1363, 1249, 1198, 1142, 1118, 1092, 1066, 983, 944, 912, 883, 862 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$, distinguishable signals of the individual diastereomers are marked by #): δ = 0.86 (s, 3H; CH_3), 0.86 (s, 3H; CH_3)#, 1.15 (s, 9H; $C(CH_3)_3$), 1.17 (s, 9H; $C(CH_3)_3$)#, 1.22–1.63 (m, 11H), 1.71–2.82 (m, 8H), 3.38–3.47 (m, 1H), 3.99 ppm (m_c, 4H; OCH_2CH_2O); ^{13}C NMR (75.5 MHz, $CDCl_3$, add. APT): δ = 11.26 (+, CH_3), 11.37 (+, CH_3), 24.75 (−, CH_2), 25.13 (−, CH_2), 25.59 (−, CH_2), 25.74 (−, CH_2), 25.94 (−, CH_2), 26.80 (−, CH_2), 28.67 (+, 3C, $C(CH_3)_3$), 29.24 (−, CH_2), 31.11 (−, CH_2), 31.21 (−, CH_2), 34.45 (+, CH), 35.13 (−, CH_2), 35.48 (−, CH_2), 35.66 (−, CH_2), 37.40 (−, CH_2), 40.79 (−, CH_2), 41.42 (−, CH_2), 41.56 (−, CH_2), 41.82 (−, CH_2), 42.70 (−, C_{quat}), 43.41 (−, C_{quat}), 45.55 (+, CH), 45.78 (+, CH), 46.72 (+, CH), 47.71 (+, CH), 58.54 (−, C_{quat}), 58.96 (−, C_{quat}), 60.36 (−, C_{quat}), 64.36 (−, OCH_2CH_2O), 72.42 (−, C_{quat}, $C(CH_3)_3$), 79.92 (+, CH, C-17), 79.98 (+, CH, C-17), 108.29 (−, C_{quat}, C-3), 108.44 (−, C_{quat}, C-3), 119.45 (−, C_{quat}), 120.73 (−, C_{quat}), 127.37 (−, C_{quat}), 128.28 (−, C_{quat}), 129.19 (−, C_{quat}), 129.54 (−, C_{quat}), 129.69 ppm (−, C_{quat}); MS (70 eV): *m/z* (%): 435/433 (1/4) [M^+], 397 (1), 379/377 (4/11) [$M^+-C_4H_8$], 341 (8), 315 (2), 289/287 (3/10), 252 (36), 246 (15), 208 (6), 166 (2), 155 (100), 133 (8), 111 (14), 96 (21), 84 (25), 57 (27) [$C_4H_9^+$], 41 (9); HRMS: *m/z*: calcd for $C_{25}H_{36}ClNO_3+H^+$ (436.0): 434.24565 (correct HRMS).

(3b*S*,9a*S*,10*S*,12a*S*,12b*R*)-10-*tert*-Butoxy-9a-methyl-2-phenyl-spiro(1′,3′-dioxolane[2′,5]-4,5,6,7,8,9,9a,10,11,12,12a,12b-dodecahydro-3b*H*-2,3a,12c-triazadicyclopenta[*a*,*l*]phenanthrene-1,3-dione) (*trans*-26): Following GP 4, a solution of the tricyclic diene *trans*-**19** (100 mg, 0.289 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (76.0 mg, 0.434 mmol) in dichloromethane (2.0 mL) was stirred at ambient temperature for 12 h. Column chromatography (32 g of silica gel, diethyl ether/pentane 1:2) provided the title product *trans*-**26** as a colorless wax (116 mg, 77 %). R_f = 0.3; $[\alpha]_D^{20}$ = +60.3 (*c* = 1.09 in MeOAc); IR (film): $\tilde{\nu}$ = 3067, 2973, 2931, 1768, 1714, 1685, 1646, 1559, 1503, 1457, 1419, 1362, 1299, 1267, 1244, 1194, 1143, 1092, 1073, 945, 911, 733 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (s, 3H; CH_3), 1.10 (s, 9H; $C(CH_3)_3$), 1.42–1.73 (m, 6H), 1.79–2.21 (m, 7H), 2.77 (m_c, 2H), 3.08 (m_c, 1H), 3.39 (t, ^3J = 7.3 Hz, 1H; 10-H), 3.90–4.08 (m, 5H), 7.27–7.53 ppm (m, 5H; Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$, add. APT): δ = 11.75 (+, CH_3), 23.90 (−, CH_2), 24.65 (−, CH_2), 25.59 (−, CH_2), 28.76 (+, 3C, $C(CH_3)_3$), 31.00 (−, CH_2), 35.87 (−, CH_2), 38.85 (−, CH_2), 41.28 (−, C_{quat}, C-13), 45.03 (−, CH_2), 52.52 (+, CH), 54.76 (+, CH), 55.50 (+, CH), 64.47 (−, 2C, CH_2, OCH_2CH_2O), 72.53 (−, C_{quat}, $C(CH_3)_3$), 79.63 (+, CH, C-10), 107.49 (−, C_{quat}, C-5), 123.57 (−, C_{quat}), 125.26 (+, CH), 127.63 (+, CH, 2C, Ph), 129.18 (+, CH, 2C, Ph), 129.75 (−, C_{quat}), 131.42 (−, C_{quat}), 149.76 (−, C_{quat}, NC=O), 153.49 ppm (−, C_{quat}, NC=O); MS (70 eV): *m/z* (%): 521.4 (100) [M^+], 465 (62) [$M^+-C_4H_8$], 420 (5), 354 (8), 345 (2), 289 (16), 289 (2), 231 (2), 178 (9), 119 (4), 99 (21), 786 (6), 57 (21) [$C_4H_9^+$], 41 (4); HRMS: *m/z*: calcd for $C_{30}H_{39}N_3O_5+H^+$ (522.7): 522.29631 (correct HRMS).

(9a*S*,10*S*,12a*R*)-10-*tert*-Butoxy-2,9a-dimethyl-spiro(1′,3′-dioxolane[2′,5]-3b,6,7,8,9,9a,10,11,12,12a,12b,12c-dodecahydro-3a*H*,4*H*-2-azadicyclopenta[*a*,*l*]phenanthrene-1,3-dione) (*cis*-23α,β): Following GP 4, a solution of the tricyclic diene *cis*-**19** (416 mg, 1.20 mmol) and *N*-methylmaleimide (187 mg, 1.50 mmol) in benzene (2.00 mL) was heated at 110 °C for 14 h. Column chromatography (25 g of silica gel, pentane/diethyl ether/methanol 1:1:0.02) provided the title compounds *cis*-**23**α,β as a colorless wax (341 mg, 62 %). R_f = 0.3; $[\alpha]_D^{20}$ = +3.20 (*c* = 1.53 in MeOAc); IR (film): $\tilde{\nu}$ = 2969, 2881, 1772, 1744, 1700, 1653, 1617, 1457, 1436, 1383, 1363, 1327, 1287, 1246, 1198, 1121, 1091, 1048, 979, 948, 902, 871, 844 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$, distinguishable signals of the individual diastereomers are marked by #): δ = 0.83 (s, 3H; CH_3), 1.00 (s, 3H; CH_3)#, 1.16 (s, 9H; $C(CH_3)_3$), 1.18 (s, 9H; $C(CH_3)_3$)#, 1.22–2.05 (m, 7H), 2.12–2.58 (m, 10H), 2.72 (m_c, 1H), 2.90 (s, 3H; NCH_3), 2.98 (s, 3H; NCH_3)#, 3.04 (m_C, 1H), 3.52 (dd, ^3J = 9.5, ^3J = 8.0 Hz, 1H; 10-H), 3.52–3.68 ppm (m, 4H; OCH_2CH_2O); ^{13}C NMR (75.5 MHz, $CDCl_3$, add. APT): δ = 22.08 (+, CH_3), 23.00 (+, CH_3)#, 23.37 (−, CH_2), 23.71 (−, CH_2)#, 24.52 (+, CH), 24.84 (+, CH)#, 25.76 (−, CH_2), 25.97 (−, CH_2)#, 26.33 (−, CH_2), 28.72 (+, 3C, $C(CH_3)_3$)#, 28.84 (+, 3C, $C(CH_3)_3$), 30.96 (−, CH_2), 31.62 (−, CH_2)#, 33.54 (+, CH), 33.91 (−, CH_2), 34.06 (−, CH_2)#, 34.72 (−, CH_2), 35.04 (+, CH)#, 35.41 (−, CH_2), 35.66 (−, CH_2)#, 36.62 (+, CH), 40.73 (+, CH)#, 41.76 (+, CH), 41.96 (+, CH)#, 42.01 (+, CH)#, 42.51 (−, C_{quat}), 42.89 (+, CH), 43.74 (−, C_{quat})#, 52.86 (+, NCH_3),

64.07 (–, CH_2, 2C, OCH_2CH_2O), 64.40 (–, CH_2, 2C, OCH_2CH_2O)#, 72.29 (–, C_{quat}, $C(CH_3)_3$), 72.55 (–, C_{quat}, $C(CH_3)_3$]#, 76.19 (+, CH, C-10), 80.36 (+, CH, C-10)#, 108.15 (–, C_{quat}, C-5), 109.91 (–, C_{quat}, C-5)#, 125.94 (–, C_{quat}), 127.97 (–, C_{quat})#, 129.77 (–, C_{quat}), 134.04 (–, C_{quat})#, 177.71 (–, C_{quat}, C=O), 177.89 (–, C_{quat}, C=O), 179.73 (–, C_{quat}, C=O)#, 179.83 ppm (–, C_{quat}, C=O)#; MS (70 eV): *m/z* (%): 457 (1) [M^+], 412 (1), 401 (64) [$M^+-C_4H_8$], 400 (22) [$M^+-C_4H_9$], 383 (10), 356 (7), 339 (22), 321 (9), 305 (4), 290 (1), 155 (2), 112 (3), 86 (5), 78 (6), 74 (26), 57 (9) [$C_4H_9^+$], 43 (100); HRMS: *m/z*: calcd for $C_{27}H_{39}NO_5+H^+$ (458.6): 458.29044 (correct HRMS).

(8a*R*,9*S*,9a*R*,12a*R*)-10,10-dimethyl-spiro(1′,3′-dioxolane[2′,12])-2,3b,4,5,6,7,8,12,12a,13,14,15,15a,15b,15c-tetradecahydro-3a*H*-2-phenyl-9,14-dioxa-[*c*]-2-azadicyclopenta[*a*,*l*]phenanthrene-1,3-dione) (27a,β): Following GP 4, a solution of the tricyclic diene **20** (60.0 mg, 0.181 mmol) and *N*-phenylmaleimide (156 mg, 0.962 mmol) in toluene (2.0 mL) was stirred at 80 °C for 20 h. Column chromatography (19 g of silica gel, pentane/diethyl ether 2:1) provided the title products **27**α,β as a colorless wax (48.5 mg, 53 %). R_f = 0.3; IR (film): $\tilde{\nu}$ = 3064, 2963, 2874, 1742, 1705, 1650, 1627, 1448, 1373, 1354, 1320, 1292, 1257, 1199, 1121, 1091, 1066, 994, 944, 912, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, distinguishable signals of the individual diastereomers are marked with "#"): δ = 1.29 (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 1.40 (s, 3H; CH_3)#, 1.49 (s, 3H; CH_3)#, 1.60–1.73 (m, 2H)#, 1.82–2.01 (m, 2H), 2.04–2.20 (m, 2H), 2.28–2.49 (m, 5H), 2.51–2.69 (m, 2H), 2.73 (dd, ^3J = 8.8, ^3J = 6.9 Hz, 1H), 3.34–3.60 (m, 4H; 2″-H, 3″-H), 4.05 (dd, ^3J = 6.9, ^3J = 2.2 Hz, 1H; 9-H), 4.83 (d, ^3J = 6.6 Hz, 1H; 8-H), 6.94–7.03 (m, 3H; Ph)#, 7.10–7.24 (m, 3H; Ph), 7.43–7.51 (m, 2H; Ph), 7.58–7.63 ppm (m, 2H; Ph)#; ^{13}C NMR (75.5 MHz, $CDCl_3$ add. APT): δ = 20.94 (–, CH_2), 21.52 (–, CH_2), 23.47 (–, CH_2), 23.69 (–, CH_2), 25.24 (+, CH_3), 27.27 (+, CH_3), 30.38 (+, CH)#, 32.52 (+, CH), 37.67 (+, CH), 39.87 (–, CH_2), 42.65 (+, CH), 43.37 (+, CH), 44.06 (–, CH_2), 45.08 (+, CH), 63.88 (–, OCH_2CH_2O), 64.35 (–, OCH_2CH_2O), 69.02 (+, CH, C-9), 74.34 (+, CH, C-8), 107.54 (–, C_{quat}, C-11), 117.02 (–, C_{quat}, C-2′), 119.63 (+, CH, Ph), 123.99 (–, C_{quat})#, 125.02 (–, C_{quat}), 125.84 (–, C_{quat})#, 127.77 (+, CH, 2C, Ph), 127.87 (+, CH, 2C, Ph)#, 128.60 (+, CH, 2C, Ph), 128.79 (+, CH, 2C, Ph)#, 133.42 (–, C_{quat}, Ph), 143.80 (–, C_{quat}), 175.82 (–, C_{quat}, C=O), 176.51 ppm (–, C_{quat}, C=O); MS (70 eV): *m/z* (%): 505 (100) [M^+], 490 (7) [M^+-CH_3], 447 (11), 403 (24), 385 (16), 361 (7), 345 (96), 318 (11), 273 (5), 199 (26), 171 (13), 157 (10), 129 (22), 99 (17), 91 (24), 87 (40), 77 (12), 67 (10); HRMS: *m/z*: calcd for $C_{30}H_{35}O_6N$ (505.6): 505.2463 (correct HRMS).

(13*S*,14*S*,17*S*)-17-*tert*-Butoxy-13-methyl-spiro(1″,3″-dioxolane[2″,3]-2,3,4,5,6,7,8,11,23,13,14,15,16,17-tetradecahydro-1*H*-(6′,6′dimethyl-4′,8′-dioxaspiro)[6′,3]cyclopropa[6,7]cyclopenta[*a*]phenanthrene) (*trans*-28): Following GP 4, a solution of the tricyclic diene *trans*-**19** (100 mg, 0.289 mmol) and 6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-ene (60.8 mg, 0.434 mmol) in benzene (1.5 mL) was stirred at 130 °C for 12 h. Column chromatography (27 g of silica gel, pentane/diethyl ether 1:1) provided a mixture of two diastereoisomers of *trans*-**28** as a colorless wax (43.6 mg, 31 %). R_f = 0.5; IR (film): $\tilde{\nu}$ = 2965, 2872, 1653, 1635, 1472, 1393, 1363, 1267, 1220, 1193, 1108, 1078, 1036, 962, 948, 898, 823, 794 cm^{-1}; ^1H NMR (300 MHz, C_6D_6, distinguishable signals of the single diastereomers are marked by #): δ = 0.73 (s, 3H; CH_3), 0.88 (s, 6H; CH_3)#, 0.98 (s, 3H; CH_3), 1.03 (s, 3H; CH_3), 1.10 (s, 9H; $C(CH_3)_3$], 1.11 (s, 9H; $C(CH_3)_3$)#, 1.14–1.25 (m, 2H), 1.32–2.22 (m, 11H), 2.38–2.70 (m, 5H), 3.33 (t, ^3J = 7.0 Hz, 1H; 17-H), 3.42–3.57 (m, 5H), 3.90–4.05 ppm (m, 4H; OCH_2CH_2O); ^{13}C NMR (75.5 MHz, $CDCl_3$, add. APT): δ = 11.53 (+, CH_3), 15.69 (+, CH_3)#, 21.41 (+, CH, Cp), 22.07 (+, CH, Cp)#, 22.23 (+, CH, Cp), 22.44 (+, CH, Cp)#, 22.74 (–, CH_2), 23.33 (+, CH)#, 23.68 (–, CH_2), 24.52 (–, CH_2)#, 25.03 (+, CH), 25.32 (–, CH_2)#, 25.70 (–, CH_2), 27.07 (–, CH_2), 27.32 (+, CH), 27.41 (+, CH)#, 28.70 (+, 3C, $C(CH_3)_3$), 28.83 (+, 3C, $C(CH_3)_3$)#, 30.18 (+, CH_3), 30.30 (+, CH_3)#, 30.84 (–, CH_2), 31.13 (–, CH_2), 31.80 (–, CH_2), 32.03 (+, CH), 34.26 (–, CH_2), 35.67 (–, CH_2), 36.79 (–, CH_2), 38.99 (–, CH_2), 41.92 (–, CH_2), 42.37 (+, CH)#, 42.60 (–, C_{quat}), 43.44 (–,C_{quat})#, 45.29 (–, C_{quat}), 52.05 (+, CH), 64.07 (–, OCH_2CH_2O)#, 64.30 (–, 2C, OCH_2CH_2O), 64.42 (–, OCH_2CH_2O)#, 71.17 (–, C_{quat}, $C(CH_3)_3$)#, 72.25 (–, C_{quat}, $C(CH_3)_3$), 75.34 (–, CH_2)#, 75.65 (–, CH_2), 75.77 (–, CH_2)#, 76.43 (–, CH_2), 80.32 (+, CH), 81.43 (+, CH)#, 89.03 (–, C_{quat}), 89.94 (–, C_{quat})#, 108.92 (–, C_{quat}), 109.07 (–, C_{quat}), 126.24 (–, C_{quat}), 127.87 (–, C_{quat}), 127.97 (–, C_{quat}), 129.79 ppm (–, C_{quat}); ESI-MS (NH_3): *m/z* (%): 990 (31), 487 (100) [M^++H]; HRMS: *m/z*: calcd for $C_{30}H_{46}O_5+H^+$ (487.6): 487.34180 (correct HRMS).

Dimethyl (13*S*,14*S*,17*S*)-17-*tert*-Butoxy-13-methyl-spiro(1′,3′-dioxolane-[2′,3]-2,3,4,5,6,7,8,11,23,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]-phenanthrene-6,7-dicarboxylate) (*trans*-29): Following GP 4, a solution of the tricyclic diene *trans*-**19** (100 mg, 0.289 mmol) and dimethyl maleate (62.6 mg, 0.434 mmol) in benzene (1.5 mL) was stirred at 130 °C for 12 h. Column chromatography (25 g of silica gel, pentane/diethyl ether 1:1) provided a mixture of two diastereoisomers of *trans*-**29** as a colorless wax (63.8 mg, 45 %). IR (film): $\tilde{\nu}$ = 2975, 1735, 1684, 1653, 1472, 1457, 1436, 1388, 1362, 1262, 1197, 1124, 1081, 1033 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$, distinguishable signals of the individual diastereomers are marked by #): δ = 0.73 (s, 3H; CH_3), 0.73 (s, 3H; CH_3), 0.86 (s, 3H; CH_3)#, 0.90 (s, 3H; CH_3)#, 1.07 (s, 9H; $C(CH_3)_3$)#, 1.09 (s, 9H; $C(CH_3)_3$), 1.13–2.16 (m, 3H), 2.35–2.81 (m, 9H), 2.92–3.04 (m, 6H), 3.23–3.39 (m, 1H), 3.60 (s, 3H; OCH_3), 3.61 (s, 3H; OCH_3)#, 3.63 (s, 3H; OCH_3), 3.67 (s, 3H; OCH_3)#, 3.68 (s, 3H; OCH_3)#, 3.88–4.03 ppm (m, 4H; OCH_2CH_2O); ^{13}C NMR (75.5 MHz, $CDCl_3$, add. APT): δ = 10.14 (s, CH_3)#, 11.99 (s, CH_3), 22.45 (–, CH_2)#, 23.60 (–, CH_2), 24.10 (–, CH_2)#, 25.60 (–, CH_2)#, 25.83 (–, CH_2), 26.10 (–, CH_2)#, 26.48 (–, CH_2)#, 28.71 (+, 3C, $C(CH_3)_3$), 30.94 (–, CH_2)#, 31.11 (–, CH_2), 31.37 (–, CH_2), 34.80 (+, CH), 35.07 (+, CH)#, 35.42 (–, CH_2)#, 35.75 (–, CH_2)#, 36.07 (–, CH_2), 36.95 (+, CH)#, 38.60 (+, CH), 39.06 (–, CH_2), 39.41 (+, CH), 39.73 (–, CH_2), 39.83 (+, CH), 41.11 (+, CH)#, 41.76 (–, CH_2)#, 42.56 (–, CH_2), 43.03 (+, CH)#, 43.79 (–, C_{quat}), 44.37 (+, CH), 44.76 (+, CH), 44.99 (+, CH)#, 45.26 (+, CH)#, 49.22 (+, CH)#, 51.45 (+, OCH_3), 51.68 (+, OCH_3), 51.82 (+, 2C, OCH_3)#, 64.14 (–, 2C, OCH_2CH_2O)#, 64.29 (–, OCH_2CH_2O), 64.35 (–, OCH_2CH_2O), 72.30 (–, C_{quat}, $C(CH_3)_3$), 79.54 (+, CH, C-17)#, 80.19 (+, CH, C-17), 108.10 (–, C_{quat}, C-3)#, 108.50 (–, C_{quat}, C-3), 125.93 (–, C_{quat})#, 126.23 (–, C_{quat})#, 126.99 (–, 2C, C_{quat}), 131.97 (–, C_{quat}), 135.29 (–, C_{quat}), 173.54 (–, C=O)#, 173.81 (–, C=O), 174.26 (–, C=O)#, 175.98 ppm (–, C=O); ESI-MS (NH_3): *m/z* (%): 1020 (67), 998 (77), 529 (38), 513 (19), 508 (92) [M+NH_4^+], 491 (100) [M+H^+], 431 (30), 375 (18); HRMS: *m/z*: calcd for $C_{28}H_{42}O_7+H^+$ (491.6): 491.30033 (correct HRMS).

(3a*R*,3b*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-*tert*-Butoxy-2,9a-dimethyl-3b,6,7,8,9,9a,10,11,12,12a,12b,12c-dodecahydro-3a*H*,4*H*-2-aza-dicyclopenta[*a*,*l*]phenanthrene-1,3,5-trione (*trans*-30): *p*-Toluenesulfonic acid (93.0 mg, 0.489 mmol) was added to a solution of the steroid analogue *trans*-**23** (700 mg, 1.53 mmol) in acetone (30 mL) and water (0.100 mL). The resulting solution was stirred at 23 °C for 24 h. The reaction mixture was concentrated in vacuo, and the residue was taken up in diethyl ether (75 mL). After washing with sat. $NaHCO_3$ solution (20 mL), the organic layer was dried over $MgSO_4$. After removal of the volatile components in vacuo, the residue was purified by column chromatography on silica gel (30 g, pentane/diethyl ether 1:2) to yield the product *trans*-**30** as a colorless wax (626 mg, 99 %). R_f = 0.4; IR (film): $\tilde{\nu}$ = 2967, 2930, 2871, 1768, 1695, 1653, 1457, 1436, 1385, 1362, 1336, 1288, 1268, 1226, 1198, 1131, 1095, 1081, 1064, 980, 963, 900, 839 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.69 (s, 3H; CH_3), 1.16 (s, 9H; $C(CH_3)_3$), 1.21–1.73 (m, 8H), 1.93–2.13 (m, 1H), 2.19–2.52 (m, 5H), 2.56–2.73 (m, 2H), 2.96–3.09 (m, 2H), 2.90 (s, 3H; NCH_3), 3.49 (m_C, 1H), 3.58 ppm (t, ^3J = 8.7 Hz, 1H; 10-H); ^{13}C NMR (75.5 MHz, C_6D_6, add. APT): δ = 11.56 (+, CH_3), 22.88 (–, CH_2), 23.18 (–, CH_2), 24.28 (+, CH), 25.25 (–, CH_2), 28.53 (+, 3C; $C(CH_3)_3$), 31.76 (–, CH_2), 34.03 (–, CH_2), 34.32 (+, CH), 38.15 (–, CH_2), 40.69 (+, CH), 40.77 (+, CH), 41.42 (–, CH_2), 42.02 (+, CH), 42.82 (C_{quat}, C-9a), 43.75 (+, CH), 72.21 (C_{quat}, $C(CH_3)_3$), 80.78 (+, CH, C-10), 130.60 (–, C_{quat}), 131.01 (–, C_{quat}), 177.08 (–, C_{quat}, NC=O), 177.45 (–, C_{quat}, NC=O), 209.33 ppm (–, C_{quat}, C=O); MS (70 eV), *m/z* (%): 413 (5) [M^+], 371 (6), 357 (100) [$M^+-C_4H_8$], 356 (21) [$M^+-C_4H_9$], 339 (82), 312 (20), 300 (17), 295 (11), 246 (28), 227 (20), 201 (6), 166 (12), 122 (4), 113 (13), 61 (8), 57 (38) [$C_4H_9^+$], 43 (29); HRMS: *m/z*: calcd for $C_{25}H_{35}NO_4+H^+$ (414.6): 414.26393 (correct HRMS).

(3a*R*,3b*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-Hydroxy-2,9a-dimethyl-3b,6,7,8,9,9a,10,11,12,12a,12b,12c-dodecahydro-3a*H*,4*H*-2-aza-dicyclopenta[*a*,*l*]phenanthrene-1,3,5-trione (*trans*-31): Trifluoroacetic acid (3.00 mL) was added to a solution of the oxosteroid analogue *trans*-

30 (237 mg, 0.573 mmol) in methylene chloride (27.0 mL), and the mixture was stirred at 23 °C for 2.0 h. After this time, the reaction mixture was concentrated in vacuo, and the residue was taken up in diethyl ether (30 mL), washed with sat. $NaHCO_3$ solution (10 mL), and dried over $MgSO_4$. After concentration in vacuo, the residue was purified by column chromatography (25 g of silica gel, diethyl ether + 3 % methanol) to yield the product *trans*-**31** as a colorless solid. M.p. 169–173 °C (186 mg, 91 %). $R_f = 0.3$; $[\alpha]_D^{20} = -16.1$ ($c = 0.981$ in MeOAc); IR (film): $\tilde{\nu} = 3370$, 2955, 2876, 1768, 1684, 1653, 1559, 1437, 1382, 1371, 1286, 1265, 1138, 1046, 1034, 983, 911, 881, 844 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.67$ (s, 3H; CH_3), 1.18–1.78 (m, 6H), 2.01–2.27 (m, 4H), 2.28–2.51 (m, 3H), 2.54–2.70 (m, 4H), 2.85 (s, 3H; NCH_3), 2.90–3.05 (m, 2H), 3.46 (dd, $^3J = 20$, $^3J = 12$ Hz, 1H), 3.82 ppm (t, $^3J = 8.0$ Hz, 1H; 10-H); ^{13}C NMR (75.6 MHz, $CDCl_3$ add. H,H-COSY, APT, HSQC, HMBC, NOESY): $\delta = 11.39$ (+, CH_3), 22.86 (–, CH_2), 23.44 (–, CH_2), 24.28 (–, CH_2), 24.69 (+, CH_3, NCH_3), 30.64 (–, CH_2), 33.12 (–, CH_2), 34.36 (+, CH), 38.11 (–, CH_2), 40.63 (+, CH), 40.66 (–, CH_2), 41.19 (–, C_{quat}, C-9a), 41.91 (+, CH), 42.71 (+, CH), 43.69 (+, CH), 81.50 (+, CH, C-10), 130.00 (–, C_{quat}), 131.27 (–, C_{quat}), 177.33 (–, C_{quat}), 177.83 (–, C_{quat}), 211.88 ppm (–, C_{quat}, C=O); MS (70 eV): *m*/*z* (%): 357 (100) [M^+], 354 (46), 337 (10), 298 (14), 283 (10), 246 (100), 221 (82), 185 (11), 167 (15), 143 (14), 129 (20), 113 (62), 79 (18), 55 (30); HRMS: *m*/*z*: calcd for $C_{21}H_{27}NO_4 + H^+$ (358.4): 358.20123 (correct HRMS).

(5*R*,6*S*,7*S*,8*S*,13*S*,14*S*,17*S*)-17-*tert*-Butoxy-13-methyl-3-oxo-2,3,4,5,6,7,8,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-6,7-dicarbonitrile (*trans*-32): *p*-Toluenesulfonic acid (80.0 mg, 0.402 mmol) was added to a solution of the steroid analogue *trans*-**22** (330 mg, 777 mmol) in acetone (15.0 mL) and water (0.050 mL). The resulting solution was stirred at 23 °C for 24 h. After this time, the reaction mixture was concentrated in vacuo, and the residue was taken up in diethyl ether (55 mL). After washing the solution with sat. $NaHCO_3$ solution (15 mL), the organic layer was dried over $MgSO_4$. After removal of the volatile components in vacuo, the residue was purified by column chromatography (30 g of silica gel, pentane/diethyl ether 1:2) to yield the product *trans*-**32** as a colorless wax (252 mg, 85 %). $R_f = 0.3$; IR (film): $\tilde{\nu} = 2974$, 2931, 2874, 2267, 1715, 1637, 1508, 1461, 1444, 1389, 1363, 1337, 1294, 1253, 1196, 1137, 1099, 1082, 1058, 1016, 969, 942, 832 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.87$ (s, 3H; CH_3), 1.15 (s, 9H; C-$(CH_3)_3$), 1.18–1.26 (m, 1H), 1.31–1.64 (m, 3H), 1.73 (m_c, 1H), 1.80–1.89 (m, 1H), 1.92–2.05 (m, 1H), 2.18 (m_c, 2H), 2.32–2.43 (m, 1H), 2.49–2.63 (m, 3H), 2.71–2.89 (m, 2H), 2.96–3.06 (m, 2H), 3.11–3.19 (m, 2H), 3.44 ppm (t, $^3J = 7.5$ Hz, 1H, 17-H); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): $\delta = 10.70$ (+, CH_3), 23.63 (–, CH_2), 24.34 (–, CH_2), 27.33 (–, CH_2), 28.63 (+, 3C; C(CH_3)$_3$), 29.18 (+, CH), 30.83 (–, CH_2), 31.32 (+, CH), 35.75 (–, CH_2), 36.19 (+, CH), 38.31 (+, CH), 40.58 (C_{quat}, C-13), 42.46 (–, CH_2), 46.85 (+, CH), 47.48 (–, CH_2), 72.58 (–, C_{quat}, *C*(CH_3)$_3$], 79.88 (–, C_{quat}, $CO_2C(CH_3)_3$), 118.11 (–, C_{quat}, CHCN), 118.65 (–, C_{quat}, CHCN), 125.59 (–, C_{quat}), 130.33 (–, C_{quat}), 207.20 ppm (–, C_{quat}, C=O); MS (70 eV): *m*/*z* (%): 380 (3) [M^+], 352 (2), 324 (36) [$M^+ - C_4H_8$], 306 (47), 279 (18), 265 (9), 226 (5), 180 (2), 129 (2), 91 (5), 57 (100) [$C_4H_9^+$], 41 (14); HRMS: *m*/*z*: calcd for $C_{24}H_{32}O_2N_2 + NH_4^+$ (398.5): 398.28020 (correct HRMS).

(6*S*,7*S*,5*R*,8*S*,13*S*,14*S*,17*S*)-17-Hydroxy-13-methyl-3-oxo-2,3,4,5,6,7,8,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-6,7-dicarbonitrile (*trans*-33): Trifluoroacetic acid (1.00 mL) was added to a solution of the oxosteroid analogue *trans*-**32** (150 mg, 0.395 mmol) in methylene chloride (10.0 mL), and the mixture was stirred at 23 °C for 2 h. After this time, the reaction mixture was concentrated in vacuo, and the residue was taken up in diethyl ether (35 mL), washed with sat. $NaHCO_3$ solution (10 mL), and dried over $MgSO_4$. After concentration in vacuo, the residue was purified by column chromatography (25 g of silica gel, diethyl ether + 1 % methanol) to yield the product *trans*-**33** as a colorless solid. M.p. 188–190 °C (120 mg, 94 %); $R_f = 0.3$; $[\alpha]_D^{20} = -4.80$ ($c = 1.02$ in MeOAc); IR (film): $\tilde{\nu} = 3410$, 2955, 2878, 2253, 1734, 1669, 1635, 1472, 1457, 1437, 1371, 1339, 1254, 1133, 1072, 1047, 981, 942, 915, 845, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 0.89 (s, 3H; CH_3), 1.22 (m_c, 1H), 1.35–1.71 (m, 3H), 1.77 (m_c, 1H), 1.90 (m_c, 1H), 2.08–2.27 (m, 3H), 2.30–2.46 (m, 1H), 2.49–2.60 (m, 3H), 2.72–2.93 (m, 3H), 2.97–3.08 (m, 2H), 3.11–3.20 (m, 2H), 3.76 ppm (t, $^3J =$ 7.2 Hz, 1H; 17-H); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): $\delta = 10.20$ (+, CH_3), 23.22 (–, CH_2), 24.27 (–, CH_2), 27.32 (–, CH_2), 29.15 (–, CH_2), 30.25 (–, CH_2), 31.30 (+, CH), 35.35 (–, CH_2), 36.20 (+, CH), 38.27 (+, CH), 40.50 (–, CH_2), 42.94 (–, CH_2), 46.90 (+, CH), 47.42 (–, C_{quat}, C-13), 80.85 (+, CH, C-17), 117.94 (–, C_{quat}), 118.60 (–, C_{quat}), 126.00 (–, C_{quat}), 129.78 (–, C_{quat}), 207.15 ppm (–, C_{quat}, C=O); MS (70 eV): *m*/*z* (%): 324 (100) [M^+], 291 (11), 265 (15), 252 (9), 226 (11), 195 (8), 129 (9), 111 (10), 84 (18), 55 (12), 41 (17); HRMS: *m*/*z*: calcd for $C_{20}H_{24}N_2O_2 + H^+$ (325.4): 325.19113 (correct HRMS).

(3a*R*,3b*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-*tert*-Butoxy-5-methoxy-2,9a-dimethyl-3b,6,7,8,9,9a,10,11,12,12a,12b,12c-dodecahydro-3a*H*,4*H*-2-azacyclopropa[5,6]dicyclopenta[*a*,*l*]phenanthrene-1,3-dione (34): A solution of diethylzinc (2.24 mL, 2.24 mmol, 1.00 M in hexane) in CH_2Cl_2 (10 mL) was carefully treated with trifluoroacetic acid (255 mg, 2.24 mmol) at 0 °C. The resulting mixture was stirred for 20 min. After dropwise addition of diiodomethane (600 mg, 2.24 mmol), the reaction mixture was stirred until a homogeneous solution had formed. The oxosteroid analogue *trans*-**30** (92.9 mg, 0.224 mmol) was added as a solution in diethyl ether (2.0 mL), and the resulting solution was stirred at 0 °C for 1 h, and at 22 °C for 12 h. After his time, the reaction mixture was poured into sat. NH_4Cl solution and extracted with diethyl ether (35 mL). The organic layer was washed with water (20 mL) and dried over $MgSO_4$. After concentration in vacuo, the residue was purified by column chromatography on silica gel (15 g, pentane/diethyl ether 1:2) to yield the title compound **34** as a colorless wax (73.1 mg, 74 %). $R_f = 0.6$; $[\alpha]_D^{20} = -4.7$ ($c = 0.68$ in MeOAc); IR (film): $\tilde{\nu} = 2973$, 2931, 1700, 1653, 1635, 1457, 1437, 1419, 1387, 1363, 1288, 1255, 1195, 1080, 1034, 901 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.52$ (t, $^3J = 5.8$ Hz 1H; *c*-Pr-H), 0.60 (s, 3H; CH_3), 0.80 (dd, $^3J = 11.0$, $^3J = 5.9$ Hz, 1H; *c*Pr-H), 1.11 (s, 9H; C-$(CH_3)_3$), 1.18–1.37 (m, 3H), 1.42–1.79 (m, 4H), 1.90–2.21 (m, 8H), 2.53 (m_c, 1H), 2.84 (s, 3H; NCH_3), 2.93 (dd, $^3J = 8.9$, $^3J = 5.7$ Hz, 1H), 3.11 (dd, $^3J = 9.0$, $^3J = 6.3$ Hz, 1H), 3.34 (s, 3H; OCH_3), 3.53 ppm (t, $^3J =$ 7.1 Hz, 1H; 10-H); ^{13}C NMR (75.6 MHz, $CDCl_3$ add. APT, HSQC): $\delta =$ 10.76 (+, CH_3), 12.21 (–, CH_2, *c*Pr), 21.68 (+, CH, *c*Pr), 22.71 (–, CH_2), 23.03 (–, CH_2), 23.22 (–, CH_2), 24.56 (+, NCH_3), 25.02 (–, CH_2), 28.71 (+, 3C, C(CH_3)$_3$), 31.18 (–, CH_2), 33.60 (–, CH_2), 36.94 (+, CH), 40.61 (+, CH), 40.68 (+, CH), 42.04 (+, CH), 42.18 (–, C_{quat}, C-9a), 45.91 (+, CH), 53.78 (+, OCH_3), 61.93 (–, C_{quat}, C-5), 72.31 (C_{quat}, *C*(CH_3)$_3$), 80.30 (+, CH, C-10), 127.79 (–, C_{quat}), 131.82 (–, C_{quat}), 177.54 (–, C_{quat}, C=O), 178.19 ppm (–, C_{quat}, C=O); MS (70 eV): *m*/*z* (%): 441 (75) [M^+], 426 (5) [$M^+ - CH_3$], 409 (14) [$M^+ - CH_3OH$], 384 (12) [$M^+ - C_4H_9$], 353 (15), 337 (20), 330 (100), 320 (26), 308 (9), 273 (82), 255 (9), 223 (4), 192 (8), 162 (13), 123 (8), 112 (18), 91 (9), 57 (74) [$C_4H_9^+$], 41 (21); HRMS: *m*/*z*: calcd for $C_{27}H_{39}NO_4 + H^+$ (442.6): 442.29560 (correct HRMS).

(3a*R*,3b*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-Hydroxy-2,9a-dimethyl-3b,6,7,8,9,9a,10,11,12,12a,12b12c-dodecahydro-3a*H*,4*H*-2-azacyclopropa-[5,6]dicyclopenta[*a*,*l*]phenanthrene-1,3,5-trione (35) and (3a*R*,3b-*S*,9a*S*,10*S*,12a*S*,12b*R*,12c*S*)-10-Hydroxy-2,6,9a-trimethyl-3b,6,7,8,9,9a,10,11,12,12a,12b,12c-dodecahydro-3a*H*,4*H*-2-azadicyclopenta[*a*,*l*]phenanthrene-1,3,5-trione (36): Trifluoroacetic acid (0.500 mL) was added to a solution of the cyclopropasteroid analogue **34** (40.2 mg, 0.0910 mmol) in methylene chloride (5.00 mL), and the mixture was stirred at 23 °C for 2 h. After this time, the reaction mixture was concentrated in vacuo, and the residue was taken up in diethyl ether (30 mL), washed with sat. $NaHCO_3$ solution (10 mL), and dried over $MgSO_4$. After concentration in vacuo, the residue was purified by column chromatography (20 g of silica gel, diethyl ether) to yield the products **35** (14.1 mg, 40 %) and **36** (4.2 mg, 12 %) as colorless waxes.

*Compound **35***: $R_f = 0.5$; IR (film): $\tilde{\nu} = 3403$, 2924, 2865, 1695, 1653, 1636, 1465, 1436, 1383, 1336, 1287, 1266, 1213, 1169, 1131, 1081, 1054, 1033, 973, 917, 734 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.54$ (t, $^3J = 6.6$ Hz, 1H; *c*Pr-H), 0.63 (s, 3H; CH_3), 0.82 (dd, $^3J = 10.9$, $^3J = 6.0$ Hz, 1H; *c*PrH), 1.16–1.40 (m, 3H), 1.42–1.76 (m, 4H), 1.97–2.29 (m, 8H), 2.37–2.44 (m, 1H), 2.53 (m_c, 1H), 2.87 (s, 3H; NCH_3), 2.95 (dd, $^3J = 9.1$, $^3J = 6.0$ Hz, 1H), 3.11 (dd, $^3J = 9.0$, $^3J = 6.1$ Hz, 1H), 3.38 (s, 3H; OCH_3), 3.80 ppm (t, $^3J = 7.8$ Hz, 1H; 10-H); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): $\delta =$ 10.49 (+, CH_3), 12.23 (–, CH_2, *c*Pr), 21.66 (+, CH, *c*Pr), 22.72 (–, CH_2), 23.03 (–, CH_2), 23.05 (–, CH_2), 24.51 (–, CH_2), 24.61 (+, CH_3, NCH_3),

30.67 (–, CH_2), 33.23 (–, CH_2), 37.01 (+, CH), 40.48 (+, CH), 40.75 (+, CH), 42.01 (+, CH), 42.62 (–, C_{quat}, C-13), 45.87 (+, CH), 53.83 (+, OCH_3), 61.92 (–, C_{quat}, C-6), 81.44 (+, CH, C-10), 128.14 (–, C_{quat}), 131.46 (–, C_{quat}), 177.46 (–, C_{quat}, C=O), 178.03 ppm (–, C_{quat}, C=O); MS (70 eV): *m*/*z* (%): 385 (48) [M^+], 353 (21) [M^+-CH_3OH], 294 (1), 283 (2), 274 (100), 259 (10), 215 (3), 162 (4), 129 (4), 112 (6), 77 (2), 43 (2); HRMS: *m*/*z*: calcd for $C_{23}H_{31}NO_4+H^+$ (386.5): 386.23258 (correct HRMS).

Compound ***36***: $R_f=0.6$; IR (film): $\tilde{\nu}=3432$, 2967, 2874, 1684, 1653, 1457, 1436, 1419, 1384, 1339, 1287, 1265, 1215, 1163, 1133, 1088, 1058, 1038, 912, 732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.64$ (s, 3H; CH_3), 1.23 (d, $^3J=6.0$ Hz, 3H; CH_3), 1.28–1.77 (m, 4H), 1.62 (m_c, 2H), 2.01–2.21 (m, 5H), 2.22–2.80 (m, 4H), 2.69 (m_c, 1H), 2.86 (s, 3H; NCH_3), 3.00 (dd, $^3J=9.1$, $^3J=6.0$ Hz, 1H), 3.20 (dd, $^3J=9.3$, $^3J=5.4$ Hz, 1H), 3.58 (q, $^3J=5.9$ Hz, 1H; 6-H), 3.82 ppm (t, $^3J=7.2$ Hz, 1H; 10-H); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): $\delta=11.52$ (+, CH_3), 11.67 (+, CH_3), 22.62 (–, CH_2), 23.33 (–, CH_2), 24.23 (–, CH_2), 24.67 (+, NCH_3), 30.72 (–, CH_2), 33.09 (–, CH_2), 37.84 (–, CH_2), 40.39 (+, CH), 40.64 (+, CH), 41.25 (+, CH), 41.82 (+, CH), 41.95 (+, CH), 42.72 (–, C_{quat}, C-13), 42.80 (+, CH), 81.61 (+, CH, C-10), 130.45 (–, C_{quat}), 131.02 (–, C_{quat}), 177.38 (–, C_{quat}, NC=O), 177.58 (–, C_{quat}, NC=O), 213.50 ppm (–, C_{quat}, C=O); DCI-MS (NH_3): *m*/*z* (%): 389 (100) [M^++NH_4], 372 (3) [M^++H], 266 (2); HRMS: *m*/*z*: calcd for $C_{22}H_{29}NO_4+H^+$ (371.5): 372.21696 (correct HRMS).

Dimethyl (13*R*,14*S*,17*S*)-17-*tert*-Butoxy-13-methyl-spiro(1′,3′-dioxolane-[2′,3]-2,3,4,5,8,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthrene-6,7-dicarboxylate) (38) and dimethyl (14*S*,17*S*)-17-*tert*-butoxy-13-methyl-spiro(1′,3′-dioxolane[2′,3]-2,3,4,5,8,11,12,13,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthrene-6,7-dicarboxylate) (39): A solution of the aromatic steroid analogue *trans*-**24** (50.0 mg, 0.102 mmol) and DDQ (24.3 mg, 0.107 mmol) in dioxane (1.50 mL) was stirred at 100 °C for 1 h. After his time, the reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography (20 g of silica gel, pentane/diethyl ether 1:1) to yield the products **38** (34.2 mg, 69 %) and **39** (2.5 mg, 5 %) as colorless waxes:

Compound ***38***: $R_f=0.4$; IR (film): $\tilde{\nu}=3064$, 2970, 2928, 1702, 1650, 1472, 1445, 1410, 1373, 1302, 1244, 1180, 1106, 1066, 944, 915, 854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.60$ (s, 3H; CH_3), 1.16 (s, 9H; C-$(CH_3)_3$), 1.22–1.71 (m, 3H), 1.88–2.05 (m, 4H), 2.59–2.88 (m, 7H), 3.21 (d, $^3J=15.9$ Hz, 1H), 3.55 (t, $^3J=6.9$ Hz, 1H; 17-H), 3.78 (s, 3H; OCH_3), 3.83 (s, 3H; OCH_3), 3.98 ppm (m_C, 4H; OCH_2CH_2O); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): $\delta=11.35$ (+, CH_3), 23.62 (–, CH_2), 25.56 (–, CH_2), 26.16 (–, CH_2), 28.69 (+, 3C; C(CH_3)$_3$), 31.22 (–, CH_2), 31.42 (–, CH_2), 33.36 (–, CH_2), 37.27 (–, CH_2), 42.33 (+, CH), 45.44 (–, C_{quat}, C-13), 52.45 (+, 2C, OCH_3), 64.52 (–, 2C, OCH_2CH_2O), 72.52 (C_{quat}, *C*-$(CH_3)_3$), 79.33 (+, CH, C-17), 107.38 (–, C_{quat}, C-3), 129.20 (–, C_{quat}), 129.78 (–, C_{quat}), 129.98 (–, C_{quat}), 135.04 (–, C_{quat}), 135.83 (–, C_{quat}), 138.74 (–, C_{quat}), 168.95 (–, C_{quat}, C=O), 170.50 ppm (–, C_{quat}, C=O); ESI-MS (NH_3): *m*/*z* (%): 990 (49), 504 (100) [M^++NH_4], 455 (75), 397 (11); HRMS: *m*/*z*: calcd for $C_{28}H_{38}O_7+NH_4^+$ (504.6): 504.29604 (correct HRMS).

Compound ***39***: $R_f=0.4$; IR (film): $\tilde{\nu}=3073$, 2972, 2931, 1734, 1653, 1635, 1472, 1437, 1419, 1388, 1362, 1302, 1252, 1198, 1172, 1109, 1078, 1062, 1035, 947, 908, 856 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.93$ (s, 3H; CH_3), 1.18 (s, 9H; C(CH_3)$_3$), 1.60–1.81 (m, 2H), 1.86 (t, $^3J=6.3$ Hz, 2H), 2.30–2.40 (m, 1H), 2.43–2.97 (m, 6H), 3.21 (d, $^3J=17.4$ Hz, 1H), 3.76 (s, 3H; OCH_3), 3.82 (s, 3H; OCH_3), 3.84 (t, $^3J=6.6$ Hz, 1H; 17-H), 3.99 (m_c, 4H; OCH_2CH_2O), 5.58 ppm (m_c, 1H; 15-H); ^{13}C NMR (75.6 MHz, $CDCl_3$, add. APT): $\delta=16.82$ (+, CH_3), 24.65 (–, CH_2), 26.14 (–, CH_2), 28.71 (+, 3C, C(CH_3)$_3$), 30.94 (–, CH_2), 34.60 (–, CH_2), 37.23 (+, CH), 39.51 (–, C_{quat}, C-13), 46.39 (–, CH_2), 52.29 (+, OCH_3), 52.37 (+, OCH_3), 64.37 (–, OCH_2CH_2O), 64.39 (–, OCH_2CH_2O), 72.69 (–, C_{quat}, *C*(CH_3)$_3$), 79.97 (+, CH, C-17), 107.31 (–, C_{quat}, C-3), 122.50 (+, CH, C-15), 128.53 (–, C_{quat}), 129.07 (–, C_{quat}), 129.58 (–, C_{quat}), 131.42 (–, C_{quat}), 135.42 (–, C_{quat}), 138.33 (–, C_{quat}), 142.59 (–, C_{quat}), 168.40 (–, C_{quat}, C=O), 170.31 ppm (–, C_{quat}, C=O); DCI-MS (NH_3): *m*/*z* (%): 502 (100) [M+NH_4^+], 446 (3), 428 (1), 296 (1); HRMS: *m*/*z*: calcd for $C_{28}H_{36}O_7+NH_4^+$ (502.6): 502.28030 (correct HRMS).

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